PRACTICAL LEATHER CHEMISTRY

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A HANDBOOK OF LABORATORY NOTES AND METHODS FOR THE USE OF STUDENTS AND WORKS' CHEMISTS

BY

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PREFACE

ALTHOUGH this laboratory manual has been designed in the first instance for the student of chemistry specialising in the leather industry, it will, it is hoped, also be of use to the works chemist. During the last few years there have been published in such journals as the *Collegium*, *Journal of the Society of Leather Trades' Chemists* and the *Journal of the American Leather Chemists Association* a large number of important papers dealing with methods of chemical analysis as applied to the leather trade. As a consequence, existing text books on this subject are becoming somewhat out of date. With this point in mind, the author has made full use of the above publications, and referred to the more important papers contained therein in the present work. In this connection it is hoped that the list of references given at the end of each chapter will be of use to the student wishing to go further into any particular point.

The writer would here take the opportunity of impressing upon the mind of the student the necessity of constant reference to such journals as those mentioned above, as it is only by so doing can he expect to keep himself in touch with such progress as is continually being made. For the use of the reader in making notes relevant to such, a few blank sheets have been left at the end of each chapter.

In conclusion, the author wishes to express his best thanks to Mr. A. B. Bradley for his assistance during the writing of this book, while thanks are also due to Messrs. A. Hilger, Ltd., for the loan of the block for Fig. 7.

A. H.

LONDON, S.W.

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ABBREVIATIONS USED IN THIS VOLUME

COLL.	Collegium.
COLL. (LOND. EDIT.) . .	Collegium. London Edition.
J.C.S.	Journal Chemical Society.
J.S.C.I.	Journal of the Society of Chemical Industry.
J. IND. ENG. CHEM. . .	Journal of Industrial and Engineering Chemistry.
J. SOC. DYERS COLS. . .	Journal Society of Dyers and Colourists.
JOUR. SOC. LEATHER TRADES CHEM.	Journal of the Society of Leather Trades' Chemists.
JOUR. AMER. LEATHER CHEM. ASSOC.	Journal of the American Leather Chemists Association.
CHEM. ZEIT.	Chemiker Zeitung.
ZEIT. ANGEW. CHEM. . .	Zeitschrift fur angewandte Chemie.
ANN. CHIM. ANALYT. . .	Annales de Chimie Analytique.
ANN. DI CHIM. APPL. . .	Annali di Chimica Applicata.

PRACTICAL LEATHER CHEMISTRY

CHAPTER I

WATER ANALYSIS

THE following determinations are usually carried out when examining a water for its suitability either for tanning or leather dyeing purposes. In order to detect the presence of putrefactive organisms, which are, to say the least, very undesirable in a water to be used in the tanning industry, a bacteriological examination should be made. Such methods are to be found in any reliable text-book on applied bacteriology, for, as will be readily understood, this subject could not be suitably dealt with in a brief chapter.

Total Dissolved Solids.—250 c.cs. to 500 c.cs. of the filtered water, according to the amount of total solids suspected to be present, are carefully evaporated to dryness in a weighed platinum dish. The evaporation is best conducted over a small rose flame until only a small volume of water is left, and finally taken to complete dryness on a water bath. The residue is then dried in a hot air oven at 105° C. for three hours, when it is cooled in a desiccator and weighed. From the weight of total solids obtained, the quantity present in 100,000 parts of water is calculated.

Loss on Ignition of Total Solids.—The loss on ignition of the total solids gives an approximate indication of the amount of organic matter present.

The residue from the determination of the total dissolved solids is carefully ignited over a small rose flame until all organic matter has been driven off. This will be made evident by the disappearance of all black particles of carbonaceous matter. The basin is then allowed to cool, when the residue is treated with a few drops of a solution of ammonium carbonate. This is necessary, in order to reconvert any MgO or CaO formed back again into the

carbonate. The basin is again gently ignited to drive off the excess of ammonium carbonate, and then cooled in the desiccator and weighed. The loss in weight sustained by this ignition can, for technical purposes, be taken as representing organic matter.

According to Pearman and Moor,[1] the loss on ignition of a good water will seldom exceed 20 per cent. of the total solids.

Iron.—The non-volatile solids from the above determination is treated with a few drops of pure HNO_3 (free from iron), warmed, diluted with distilled water, transferred to a 100 c.c. Nessler tube and made up to the 100 c.c. mark with water. 2 c.cs. of a 5 per cent. solution of potassium sulphocyanide is added, when the presence of iron will be indicated by the formation of a blood-red coloration.

Should more than a moderate colour be produced, it will be necessary to dilute the 100 c.c. to 200 c.c. or more, so that 100 c.c. can be more accurately matched. Such dilution must be allowed for when calculating the result. The quantity present can be estimated colorimetrically by matching against a standard iron solution

To prepare the standard iron solution, 0·7 gm. of pure ferrous ammonium sulphate (this salt contains one-seventh of its weight of iron) is dissolved in a few cubic centimetres of water, and the iron oxidised to the ferric condition by warming with a few drops of HNO_3. The solution is then made up to 1000 c.cs. in a graduated flask with distilled water. 1 c.c. of this solution = 0·0001 gm. Fe.

By noting the volume of this solution required to produce the same tint as that in the water under examination, the amount of iron present can be calculated.

In order to obtain good results, the standard iron solution should be diluted to the 100 c.cs. mark on the Nessler tube before the 2 c.cs. of potassium sulphocyanide is added. Also, when judging the colours, the tubes should be held about an inch above a white surface, and the colour determined by looking down the tube.

The following examples will illustrate the method of determination :—

Example 1.—500 c.cs. of the water evaporated, etc., and the residue dissolved in HNO_3 and made up to 100 c.cs. in Nessler glass. On adding the potassium sulphocyanide a deep red colour, too deep for matching, was produced.

50 c.cs. of the solution was further diluted to 100 c.cs. with water and 1 c.c. of potassium sulphocyanide added.

This was then matched against the standard iron solution.

Iron solution required = 2·1 c.cs.

Now 1 c.c. standard iron solution = 0·0001 gm. Fe.

∴ 2·1 c.cs. = (2·1 × 0·0001) gm. Fe.

= 0·00021 gm. Fe.

Now the 50 c.cs. of solution taken for further diluting corresponds to half of the original volume of water (500 c.cs.) = 250 c.cs.

∴ 250 c.cs. water contain 0·00021 gm. Fe.

100,000 c.cs. water contain 0·084 gm.

Example 2.—500 c.cs. water treated for iron determination by the above method.

Iron solution required = 0·8 c.cs.

Now 1 c.c. of iron solution = 0·0001 gm. Fe.

∴ 0·8 c.c. „ = (0·8 × 0·0001) gm. Fe.

= 0·00008 gm. Fe.

500 c.cs. water contain = 0·00008 gm. Fe.

100,000 c.cs. „ = 0·016 gm. Fe.

Temporary Hardness.—The temporary hardness is due to the presence of dissolved bi-carbonates of calcium and magnesium, and is most conveniently estimated by Hehner's method. This consists in titrating the alkalinity produced by the bi-carbonates with $\frac{N}{10}$ acid, using methyl orange as indicator.

$$CaH_2(CO_3)_2 + H_2SO_4 = CaSO_4 + 2CO_2 + 2H_2O$$
$$MgH_2(CO_3)_2 + H_2SO_4 = MgSO_4 + 2CO_2 + 2H_2O$$

Although actually due to bi-carbonates, the temporary hardness is always expressed in terms of $CaCO_3$.

100 c.cs. of the water is pipetted into a clean conical flask, two drops of methyl orange solution added, and titrated with $\frac{N}{10}$ H_2SO_4 or HCl. To obtain greater accuracy, the volume of acid required to change the indicator from yellow to red should be determined by a blank experiment, using distilled water in place of the water under examination, with two drops of the *same* methyl orange solution. This amount is deducted from the total found in the actual titration, the difference being due to the temporary hardness in the volume of water taken. Each cubic centimetre of $\frac{N}{10}$ acid required = 0·005 gm. of $CaCO_3$, or using 100 c.cs. of the water for the

determination as already described, each cubic centimetre of acid is equivalent to 5 parts of temporary hardness per 100,000 of water.

Bennett[2] recommends the following procedure when estimating the temporary hardness of very hard waters:—

100 c.cs. of the water is titrated at the boil with $\frac{N}{10}$ acid, using methyl red as indicator. Boiling is necessary in order to expel CO_2. Another method, suggested by Winkler[3] is to boil 100 c.cs. of the water with 1–2 gms. of pure boric acid, cool and then titrate in the ordinary way with acid, using methyl orange as indicator.

Alizarin is sometimes used as the indicator, with which, it is said, very accurate results can be obtained. A few drops of a 2 per cent. alizarin paste is added to 100 c.cs. of the water. It is then titrated with $\frac{N}{10}$ acid until the violet colour turns to yellow, when the water is boiled and the titration continued until the yellow colour is permanent. It is necessary in this case to make a blank experiment to allow for the acid required to change indicator.

Permanent Hardness.—The permanent hardness is due to the dissolved sulphates of calcium and magnesium, and the method usually adopted for their estimation in works' practice is that introduced by Pfeifer and Wartha. As a matter of convenience, the permanent hardness is also expressed in terms of $CaCO_3$, in the same manner as the temporary. 200 c.cs. of the water is boiled in a conical flask with exactly 50 c.cs. of an equal mixture of $\frac{N}{10}NaOH$ and $\frac{N}{10}Na_2CO_3$ until the liquid is reduced to about two-thirds of the original volume. The solution should be boiled gently and loss by spirting guarded against by placing a funnel in the neck of the flask.

During boiling, the following reactions take place:—

$$MgSO_4 + 2NaOH = Mg(OH)_2 + Na_2SO_4$$
$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4$$

After boiling, the liquid is cooled, transferred to a 200 c.c. graduated flask and made up to the mark with distilled water. After well shaking, it is filtered, and 100 c.cs. of the filtrate (corresponding to 100 c.cs. of original water and 25 c.cs. of the mixed alkali solution) titrated with $\frac{N}{10}HCl$ or H_2SO_4, using here methyl orange as indicator. Then the number

of cubic centimetres of acid required in titrating back the unused alkali subtracted from 25 c.cs., will give the volume of $\frac{N}{10}$ alkali used in decomposing the permanent hardness in 100 c.cs. of the water. Each cubic centimetre is equivalent to 0·005 gm. of $CaCO_3$, or, if the above details are adhered to, 5 parts of permanent hardness per 100,000 parts of water.

Sodium Carbonate.—This can only be present in waters which are free from permanent hardness, and in such waters the amount of acid required in titrating back the added alkali in the estimation of the permanent hardness as already described, will exceed 25 c.cs. The excess over and above 25 c.cs. will correspond to the Na_2CO_3 present in 100 c.cs. of the water. Each cubic centimetre of excess acid is equal to 0·0053 gm. of Na_2CO_3, or 5·3 parts per 100,000 of water. It must be remembered that if sodium carbonate is present, it will also have been previously titrated when estimating the temporary hardness, so that the amount of acid corresponding to the carbonate found must be allowed for in calculating the temporary hardness.

Magnesia Hardness.—The hardness due to magnesium salts will have already been determined, either in the temporary or permanent hardness or both. It may, however, be determined separately by the following method :—

100 c.cs. of the water is neutralised with $\frac{N}{10}$ acid (the amount found necessary in the estimation of the temporary hardness), and boiled down to about 70 c cs. By this means all magnesium (and calcium) salts due to temporary hardness are converted into permanent hardness, and the magnesium can be precipitated by the addition of lime water in the form of magnesium hydrate, the calcium salts remaining unaffected.

$$MgSO_4 + Ca(OH)_2 = Mg(OH)_2 + CaSO_4$$
$$MgCl_2 + Ca(OH)_2 = Mg(OH)_2 + CaCl_2$$

After transferring the boiled water to a 200 c.c. measuring flask, 100 c.cs. of freshly filtered lime water is added, and the whole heated to 100° C. on a water bath for quarter of an hour, during which time the mouth of the flask should be covered with a watch glass so as to prevent access of atmospheric carbon-di-oxide to the lime water. In the meantime, the actual alkalinity of 50 c.cs. of the same lime water should be determined by titration with $\frac{N}{10}$ acid, using phenol phthalein as indicator.

After quarter of an hour at 100° C. the flask is cooled down, and the contents made up to the mark with distilled water. The whole is well shaken and allowed to stand for a time, when 100 c.cs. of the clear supernatent liquor is pipetted out carefully and titrated with $\frac{N}{10}$ acid, using phenol phthalein as indicator. This titration will, of course, correspond to 50 c.cs. of original water and 50 c.cs. of lime water. The reading obtained, deducted from the $\frac{N}{10}$ acid value of 50 c.cs. of lime water, will give the number of cubic centimetres of acid corresponding to the lime water used up in precipitating the magnesia in 50 c.cs. of the water. From the reading obtained, the magnesia per 100,000 parts of water can be calculated—

$$1 \text{ c.c. } \frac{N}{10} \text{ acid} = 0{\cdot}002 \text{ gm. MgO.}$$

One of the several methods suggested by Jensen [4] for the volumetric estimation of magnesium in water is as follows :—

The total solids from a known volume of the water is dissolved in HCl, and the calcium salts precipitated with ammonium oxalate and filtered off in the usual way. The filtrate is evaporated to dryness and ignited to decompose the ammonium salts. The residue is dissolved in a small quantity of dilute HCl, filtered and rendered alkaline with ammonia. The magnesium is then precipitated as magnesium ammonium arsenate by the addition of a slight excess of sodium arsenate solution. After standing overnight, the precipitate is filtered off, washed with dilute ammonia and then 50 per cent. alcohol, until the washings are free from ammonia. The washed precipitate is dissolved in a known volume of $\frac{N}{10}$ HCl, and the excess of acid titrated back with $\frac{N}{10}$ Na_2CO_3, using methyl orange as indicator.

$$MgNH_4AsO_4 + 2HCl = MgCl_2 + NH_4H_2AsO_4$$

Each cubic centimetre of $\frac{N}{10}$ acid used up corresponds to 0·002 gm. MgO. To detect magnesium chloride, which is a very undesirable constituent in boiler waters, Bosshard and Burawzow [5] recommend evaporating a known volume of water to dryness and extracting the residue with a mixture of equal volumes of *dry* alcohol and ether. This dissolves only the $MgCl_2$ and $CaCl_2$. After filtering, the solvent is

evaporated off and the residue re-dissolved in water. The CaO and Cl are determined in this solution, and, after calculating all the CaO into $CaCl_2$, any remaining Cl is taken as being present in the form of $MgCl_2$.

Carbon-di-Oxide.—According to Winkler, free CO_2 can be detected qualitatively as follows:—10 drops of a 1 per cent. alcoholic solution of alizarin are added to 100 c.cs. of the sample.

Small quantities give a copper-red colour.
Moderate quantities give a reddish-yellow colour.
Large quantities give a yellow colour.

Quantitatively, CO_2 may be determined by titrating 100 c.cs. of the water with $\frac{N}{10} Na_2CO_3$, using phenol phthalein as indicator. This titration depends upon the fact that sodium bi-carbonate, which is neutral to the indicator, is produced according to the re-action—

$$Na_2CO_3 + H_2O + CO_2 = 2NaHCO_3$$

The titration is continued until a final pink colour is obtained. The addition of the $\frac{N}{10} Na_2CO_3$ is made very slowly, one drop at a time only, and with constant shaking.

$$1 \text{ c.c. } \frac{N}{10} Na_2CO_3 = 0{\cdot}0022 \text{ gm. } CO_2$$

Chlorides.—Chlorides are best determined volumetrically, by means of a standard solution of silver nitrate, $\frac{N}{50}$ being a convenient strength. This is prepared by dissolving exactly 3·3932 gms. of pure $AgNO_3$ in a little distilled water, and making the solution up to 1 litre. 1 c.c. of this solution = 0·00071 gm. Cl or 0·00117 NaCl.

100 c.cs. of the water are measured into a conical flask and two drops of a 5 per cent. solution of potassium chromate added as indicator. The silver nitrate is carefully added from a burette until the solution turns a permanent red colour. The volume of silver nitrate solution required multiplied by the factor given above, will give the amount of Cl or NaCl, as the case may be, in 100 c.cs. of the water, from which figure the quantity in 100,000 parts of water can be calculated.

Sulphates.—Sulphates may be estimated directly by precipitating as barium sulphate and weighing in that form.

250 c.cs. of the water is made acid by adding an excess of HCl, and then concentrated down by boiling to about 70 c.cs. 10 c.cs. of a hot 5 per cent. solution of barium chloride is added and the liquid boiled for 5–10 minutes. The precipitate of $BaSO_4$ is filtered, washed with boiling distilled water, and dried in the steam oven. It is then ignited in a weighed crucible and weighed.

$$BaSO_4 \text{ into } SO_3 = 0.3433$$

General Considerations.—For obvious reasons, water either for tanning or dyeing purposes should be as free as possible from organic matter. Especially also when it is to be used for soaking raw goods, etc. In such cases, it is not the actual organic matter which produces bad effects, but the fact that waters, rich in organic matter, form a good nutrient media for harmful and undesirable putrefactive organisms to develop.

Waters with excessive temporary hardness should be avoided, as these if used for washing limed goods are liable to produce an effect on the pelt known as "lime blast," owing to the precipitation of $CaCO_3$ and $MgCO_3$ on the pelt. The temporary hardness in water used for this purpose is generally eliminated by softening with lime added in the form of freshly-made lime water. Waters containing an excessive quantity of Na_2CO_3 also tend to cause "lime blast," and render the washing difficult. Bi-carbonates darken tan liquors, with the result that the leather produced in such liquors is dark in colour. Similar remarks apply to sodium carbonate. For a very complete account of the action of the mineral constituents of water in the extraction of tanning materials, the reader is referred to a paper by Nihoul,[6] who has carried out some very valuable work on this subject.

From the dyer's standpoint, it must be remembered also that temporary hardness causes the precipitation of the basic dyestuffs, which, as well as resulting in a loss of dye, causes uneven dyeing of the leather. Water for this purpose can be neutralised with acetic acid.

Chlorides prevent the swelling of hide substance, but up to 6 parts per 100,000 of chlorides can be taken as a reasonable limit.

Iron, if present beyond the slightest trace, will produce a decided darkening in colour of tan liquors, with the consequent darkening of the leather being tanned.

REFERENCES

[1] "The Chemical and Biological Analysis of Water," 1899.
[2] *Coll.* (London Edition), 1915, p. 237.
[3] *Zeit. angew. Chem.*, 1915, p. 48.
[4] *Abstract, J.S.C.I.*, 1916, p. 1032.
[5] *Abstract, J.C.S.*, 1913, ii. p. 245.
[6] *Coll.*, 1902, p. 80.

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CHAPTER II

ANALYSIS OF LIME

LIME to be used for depilatory purposes should be practically free from iron and contain only small amounts of silica and calcium carbonate. When examining a sample of lime the following determinations are made:—

Available Lime.—5 gms. of the powdered sample is shaken with a convenient volume (about 200 c.cs.) of a 10 per cent. cane sugar solution in a 500 c.c. graduated flask for half an hour, and the solution then made up to the 500 c.c. mark with distilled water. The whole is well shaken and filtered through a rapid filter paper. 50 c.cs. of the clear filtrate is pipetted into a clean conical flask and titrated with $\frac{N}{5}$ HCl, using phenol phthalein as indicator. The reading obtained will give the number of cubic centimetres of $\frac{N}{5}$ acid required to neutralise the free lime in 0·5 gm. of the original sample.

$$1 \text{ c.c. } \frac{N}{5} \text{ HCl} = 0{\cdot}0056 \text{ gm. CaO}$$

Insoluble Matter.—5 gms. of the sample is dissolved in HCl and the solution evaporated to dryness in a platinum dish. The residue is ignited, gently at first to avoid spirting, and afterwards strongly, in order to decompose any silicates and to render the silica insoluble. After cooling, the residue is dissolved in dilute HCl, boiled, diluted with hot distilled water, and the solution filtered through an ashless filter paper. Any insoluble matter is well washed with water and the filter paper and residue dried in the steam oven. It is then ignited and weighed in a tared crucible. This will give the sand and insoluble matter in 5 gms. of the sample.

The filtrate and washings are cooled and made up to 500 c.cs. with water.

Iron and Alumina.—50 c.cs. of the above solution (corresponding to 0·5 gm. of the original sample) is transferred to a beaker and rendered alkaline with a slight excess of ammonia. It is then boiled for 5–10 minutes, and the precipitate, consisting of iron and aluminium hydrates, is filtered off, washed with boiling distilled water, dried, ignited and weighed as Fe_2O_3 and Al_2O_3. In cases where a fairly large quantity of iron is present, it is advisable to detach the dried precipitate from the paper before ignition, as a partial reduction of the Fe_2O_3 to Fe may take place. The filter paper is ignited first, and then the precipitate added, and the whole again ignited for a short time. The crucible and its contents are cooled in the desiccator and weighed.

Total Lime.—The filtrate from the iron and alumina determination is heated to the boil and a further excess of ammonia added. The calcium is then precipitated by adding a boiling solution of ammonium oxalate as long as any precipitate is formed. It is most essential that both solutions should be boiling at the time of mixing, otherwise the calcium oxalate will be somewhat difficult to filter. After boiling for 10 minutes, the calcium oxalate is filtered off and washed thoroughly with boiling distilled water. A hole is then pierced through the apex of the filter paper and the precipitate washed into a clean flask. It is then dissolved in dilute sulphuric acid. The solution is warmed to 70° C., and titrated with $\frac{N}{10}KMnO_4$ until the pink colour of the permanganate remains just permanent.

$$Ca(COO)_2 + H_2SO_4 = CaSO_4 + (COOH)_2$$
$$5(COOH)_2 + 2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$$

The $\frac{N}{10}KMnO_4$ is prepared by dissolving 3·158 gms. of the pure salt in water and making the solution up to 1000 c.cs. The solution should be standardised against either oxalic acid or ferrous ammonium sulphate, and stored in a coloured glass bottle.

$$1 \text{ c.c. } \frac{N}{10}KMnO_4 = 0{\cdot}0028 \text{ gm. } CaO$$

As an alternative to the volumetric method, either of the following gravimetric methods may be used:—

The washed and dried calcium oxalate precipitate is ignited in a tared crucible until the weight is constant. By

strong ignition, the oxalate is converted first into carbonate and finally oxide, in which form it is weighed.

Willis[1] recommends the following procedure:—

The calcium oxalate precipitate is dried, ignited to $CaCO_3$ and cooled down. For each 0·2 gm. of $CaCO_3$ is added an excess of 0·3 gm. of ammonium sulphate, and the whole well mixed with a platinum wire. The crucible is then gently heated to drive off the ammonia, etc., and the residue of $CaSO_4$ cooled and weighed.

$$CaSO_4 \text{ into } CaO = 0{\cdot}411$$

Magnesium.—The filtrate from the calcium determination is evaporated to dryness, and the residue ignited to expel all ammonium salts. This should be carried out in the fume cupboard. The residue is dissolved in a little dilute HCl, filtered if necessary, and rendered alkaline with ammonia. If any magnesium is precipitated at this stage it should be re-dissolved in dilute HCl and the solution again made alkaline with ammonia. The magnesium is then precipitated by the addition of an excess of sodium phosphate solution. Precipitation is made in the cold, and can be hastened by vigorously stirring the solution with a glass rod. Touching the side of the beaker with the rod should be avoided as much as possible, owing to the difficulty in detaching any precipitate formed thereon.

After standing overnight in the cold, the precipitate is filtered off and washed with dilute (1 per cent.) ammonia, and dried in the steam oven. The precipitate is detached from the paper, and the latter ignited in a weighed crucible. The precipitate is then added and the whole strongly heated. This will convert the magnesium ammonium phosphate into magnesium pyrophosphate, which is then cooled in the desiccator and weighed.

$$Mg_2P_2O_7 \text{ into } MgO = 0{\cdot}3606$$

Carbonates.—If a large amount of carbonate is present, it may be determined by treating a known weight of the sample with acid and collecting and weighing the CO_2 evolved in weighed potash bulbs. As an alternative, use may be made of the Schrötter apparatus.

Loss on Ignition.—1 gm. of the sample is ignited in a tared platinum crucible until the loss in weight is constant. The loss in weight represents the sum of the free and combined moisture together with CO_2 from carbonates. For technical purposes, this determination will often give information as

useful as determining the CO_2 direct, and is a more simple determination than this latter.

Sulphates.—100 c.cs. of the original solution of the lime are heated to the boil, and a boiling solution of barium chloride containing a little ammonium chloride added. Barium sulphate is difficult to precipitate in a granular form, but if both solutions are boiling this difficulty is obviated. The ammonium chloride also assists in this respect. The barium sulphate is filtered off and washed with boiling water, and dried in the steam oven. It is then ignited in a porcelain crucible and allowed to cool. Two drops of strong H_2SO_4 are added, and the crucible again ignited to drive off the excess of acid, after which the $BaSO_4$ is weighed.

$$BaSO_4 \text{ into } SO_3 = 0{\cdot}343$$

The treatment with sulphuric acid is necessary in order to re-convert any barium sulphide formed by reduction back into the sulphate.

REFERENCE

[1] *J. Ind. Eng. Chem.*, 1917, p. 1114.

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CHAPTER III

ANALYSIS OF SODIUM AND ARSENIC SULPHIDES

COMMERCIAL sodium sulphide is prepared for the market in two forms, viz.:—

(*a*) Crystalline sodium sulphide, containing about 30 per cent. of Na_2S, and

(*b*) Concentrated or fused sodium sulphide of approximately 60–65 per cent. Na_2S.

Of the various methods suggested for the determination of soluble sulphides, titration with an ammoniacal solution of zinc sulphate (as modified by Blockey and Mehd ') appears to be the most convenient for the works' chemist, and at the same time gives very satisfactory results.

The $\frac{N}{10}$ ammoniacal $ZnSO_4$ solution is prepared by dissolving 14·35 gms. of pure $ZnSO_4 . 7H_2O$ in water and adding concentrated ammonia until the precipitate at first formed is just re-dissolved. 50 gms. of pure ammonium chloride is then added, and the whole made up to 1000 c.cs. in a graduated flask. Each cubic centimetre of this solution corresponds to 0·0039 gm. of Na_2S or 0·012 gm. of $Na_2S . 9H_2O$.

Method of Estimation.—10 gms. of the powdered sample, if crystalline, or 5 gms. if fused, are dissolved in water and the solution made up to 1000 c.cs. 25 c.cs. are pipetted out into a 200 cubic centimetre wide-mouth stoppered bottle and diluted with a little distilled water.

The $\frac{N}{10}$ zinc solution is carefully run in from a burette, well shaking after each addition, until a drop withdrawn by means of a glass rod ceases to turn black a drop of a 1 per cent. nickel sulphate solution spotted on a white glazed tile. As long as any sulphide remains unprecipitated the nickel sulphate will turn black, due to the formation of nickel sulphide. From the volume of zinc solution required, the

percentage of pure sodium sulphide in the sample can be calculated.

A method recently introduced by Swann[2] for the estimation of sulphide in sulphide dyebaths could no doubt be applied to the examination of sulphide samples, and is included here for reference. (The quantities given in the original paper are for liquors containing about 10 ozs. of sulphide per gallon.)

3 gms. of crystallised sodium sulphide or 2 gms. of the concentrated variety is dissolved in 250 c.cs. of water and 20 c.cs. of the solution measured into a 150 c.c. flask. The flask is fitted with a tap funnel and is connected up to a distillation apparatus, the receiver of which contains a known volume of $\frac{N}{10}$ iodine solution acidified with a little acetic acid. To the distillation flask is added 10–20 c.cs. of a 25 per cent. ammonium chloride solution containing 5 per cent. ammonia. The ammonium sulphide formed is distilled over into the acidified iodine solution. The distillation is conducted for 5 minutes only, at the end of which time the excess of iodine is titrated back with $\frac{N}{10}$ sodium thiosulphate solution, starch paste being used as the indicator.

$$H_2S + I_2 = 2HI + S$$

Each cubic centimetre of $\frac{N}{10}$ iodine consumed = 0·012 gm. of $Na_2S . 9H_2O$.

Free Alkali.—When sodium sulphide is dissolved in water, it is hydrolysed thus:—

$$Na_2S + H_2O = NaHS + NaOH$$

and both products can be titrated with a standard acid using methyl orange as indicator.

25 c.cs. of the solution, as made up for the $\frac{N}{10}ZnSO_4$ titration (above), is pipetted into a conical flask, a few drops of methyl orange added, and titrated with $\frac{N}{10}HCl$. If no free alkali is present, this acid reading will correspond to the zinc sulphate reading, provided, of course, that the same volume of sulphide solution is used for both titrations. If free alkali is present, as is frequently the case with old samples, the acid reading will exceed the zinc sulphate reading, and the difference between the two will be the volume

of $\frac{N}{10}$ acid required to neutralise the free alkali in the 25 c.cs. of the solution. For convenience, this alkalinity can be expressed in terms of sodium carbonate, although no doubt some of it is present as caustic alkali.

$$1 \text{ c.c. } \frac{N}{10} HCl = 0{\cdot}0053 \text{ gm. } Na_2CO_3$$

Arsenic Sulphide.—This substance, which in conjunction with lime is largely used for the unhairing of goat skins intended for glove leather, is best examined by the method recommended by Proctor.[3]

0·5 gm. of the sample is weighed into a beaker and dissolved by boiling with strong nitric acid. The solution is diluted with water, rendered alkaline by the addition of an excess of ammonia and filtered if necessary.

The arsenic is then precipitated in the form of magnesium ammonium arsenate by adding "magnesia mixture" prepared as follows:—

10 gms. of crystalline magnesium chloride is dissolved in 100 c.cs. of distilled water and 25 gms of ammonium chloride added, followed by 30 c.cs. of concentrated ammonia. This mixture is allowed to stand for two days before using, and filtered if necessary.

Proctor recommends a different mixture to that given above, but this latter gives quite satisfactory results. The precipitate of magnesium ammonium arsenate, after standing overnight in the cold, is filtered off and washed with ammonia water. It is then dried in the steam oven. When dry, the precipitate is detached from the paper as completely as possible and the paper ignited in a weighed porcelain crucible. The precipitate is then added and the crucible again ignited strongly in order to convert the magnesium ammonium arsenate into magnesium pyroarsenate $Mg_2As_2O_7$. From the weight of pyroarsenate can be calculated the weight of arsenic.

	$Mg_2As_2O_7$	into	$As = 0{\cdot}4287$
or	$Mg_2As_2O_7$	„	$As_2S_2 = 0{\cdot}6903$
or	$Mg_2As_2O_7$	„	$As_2S_3 = 0{\cdot}7935$

Non-Volatile Impurities.—The non-volatile impurities in commercial arsenic sulphides may consist of sandy matter, iron oxide, etc.

1 gm. of the sample is weighed into a crucible and ignited over a strong flame in the fume cupboard. It must be emphasised that the fumes evolved are extremely poisonous, and on this account great care must be exercised. The

residue of non-volatile matter is cooled in the desiccator and weighed. It should be ignited for a further short period in order to make sure that all volatile matter has been expelled. If this is the case, there will be no further loss on heating.

REFERENCES

1 *J.S.C.I.*, 1912, p. 369.
2 *J. Soc. Dyers Col.*, 1917, p. 146.
3 *Leather Ind. Lab. Book*, p. 57.

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CHAPTER IV

THE ESTIMATION OF NITROGEN

THE accurate determination of nitrogen affords to the leather trades' chemist a valuable means of controlling various processes in leather manufacture, as well as determining the amount of hide substance in finished leather. The most convenient method for the estimation of nitrogen in organic substances such as gelatine, leather, etc., is that devised by Kjeldahl.

This method is based on the fact that when a nitrogenous substance is heated with concentrated sulphuric acid, the organic matter is oxidised, the nitrogen being converted into ammonia, which, in the presence of an excess of acid, forms ammonium sulphate. The ammonia is liberated by the addition of an excess of caustic soda, and distilled over into a known volume of standard acid. The excess of acid is subsequently titrated back with standard alkali. The exact *modus operandi* can be best described by taking as an example the estimation of nitrogen in leather.

2·5 gms. of finely divided leather is weighed out into a Kjeldahl flask and 20 c.cs. of pure nitrogen free sulphuric acid added. The mixture is heated over a small flame until the leather has dissolved, when it is heated more strongly over an ordinary bunsen flame for about 30 minutes. This operation should be carried out in a fume cupboard with a good draught. The liquid is then allowed to cool down somewhat and 10 gms. of pure potassium sulphate and a small crystal of pure copper sulphate added. The potassium sulphate raises the temperature of the boiling mixture, and the copper sulphate acts as an accelerator or oxygen carrier. The contents of the flask are now boiled until all carbonaceous matter has been destroyed and the liquid assumes a blue colour.

After being allowed to get quite cold, the acid liquid is diluted with about 300 c.cs. of water and transferred to a

500 c.c. graduated flask and cooled under the tap. It is then made up to the mark and well shaken.

100 c.cs. of this solution are pipetted into a round-bottomed distillation flask of about 750 c.cs. capacity and diluted with 200 c.cs. of distilled water. A few glass beads (to prevent bumping) and a small piece of paraffin wax (to prevent undue frothing) are added and the flask fitted to a distillation apparatus as shown in Fig. 1.

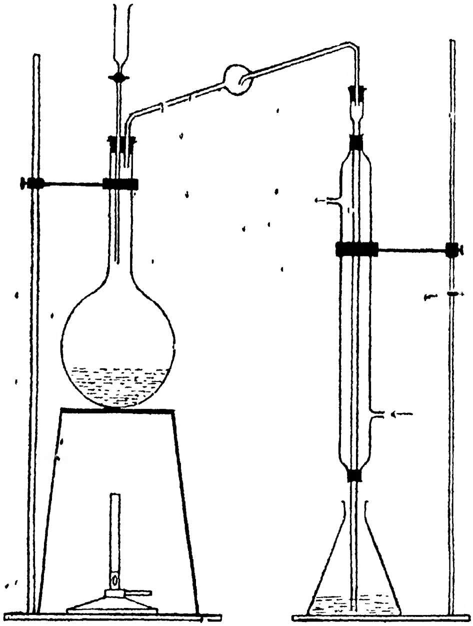

FIG. 1.—Distillation apparatus.

50 c.cs. of $\frac{N}{10} H_2SO_4$ is measured into a 300 c.c. conical flask diluted with a little distilled water and a few drops of methyl orange added as indicator. This is to absorb the ammonia evolved, and care should be taken to see that the end of the condenser tube dips well below the surface of the acid.

By means of the tap funnel, strong caustic soda solution is run into the distillation flask until the copper, which is in

solution, is precipitated. (The copper thus incidentally acts as an indicator.)

The alkaline liquid is boiled for 20 minutes, at the end of which time all the ammonia will have distilled over into the $\frac{N}{10}$ acid. The flame is then removed, the tap of the funnel opened, and the receiver removed. The condenser tube should be washed down with a little distilled water into the flask. The excess of acid in the flask is then titrated back with $\frac{N}{10}$ caustic soda.

The number of c.cs. of $\frac{N}{10}$ NaOH required, subtracted from 50, will give the volume of $\frac{N}{10}$ acid required to neutralise the ammonia produced from 0·5 gm. of leather.

$$1 \text{ c.c. } \frac{N}{10} \text{ acid} = 0{\cdot}0014 \text{ gm. N}$$

or $$= 0{\cdot}007865 \text{ gm. hide substance.}$$

Various substances other than copper sulphate can be used as accelerators, potassium permanganate being favoured by Hough.[1] This investigator adds the permanganate to the cool acid liquor after the leather has been thoroughly carbonised. He points out that it is necessary to: (1) thoroughly carbonise the leather; (2) to make the addition of permanganate at the right moment; and (3) to heat strongly immediately after the operation.

Mercury is also used as an accelerator, but is not recommended on account of the formation of mercury ammonium compounds which have to be decomposed before the ammonia is distilled. This is done by adding sodium sulphide, or, according to Sorensen,[2] by adding a little glucose, whereby the mercury is reduced to the metallic form.

Bennett[3] and Holmes have investigated the Kjeldahl method, using in their experiments pure gelatine. Their results show (using 0·25 gm. gelatine and 10 c.cs. of sulphuric acid) that the maximum amount of nitrogen is obtained only when an accelerator is used, and for this purpose they recommend K_2SO_4. Prolonged heating leads to loss of ammonia, and consequently low results. For 0·25 gm. gelatine and 10 c.cs. of H_2SO_4 the most reliable results were obtained by using 10 gms. of potassium sulphate and heating for 4–6 hours. Veitch and Trescot,[4] are of opinion that the leather

should be digested for six hours in order to give concordant results. Instead of using $\frac{N}{10}$ acid for the collection of the ammonia, a saturated solution of boric acid may be used (Winkler).[5] 50–60 c.cs. of the saturated boric acid is introduced into the receiver and a few drops of Congo red solution added as indicator. After distillation, the ammonia collected is titrated direct with $\frac{N}{10}$ acid. Congo red gives a red colour with alkalies and a blue with acids. This modification can be recommended as giving good results, and has been used for several years by the author.

REFERENCES

1 *Coll.* (London Edition), 1915, p. 126.
2 *Jour. Soc. Leather Trades Chem.*, 1918, p. 290.
3 *Ibid.*, 1919, p. 24.
4 *Jour. Amer. Leather Chem. Assoc.*, 1907, p. 221.
5 *Abstract*, *J.C.S.*, ii. 1913, p. 527.

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LEATHER CHEMISTRY

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CHAPTER V

ANALYSIS OF LIME LIQUORS

THE determination of the various constituents of a used lime liquor is a matter of considerable difficulty, owing to the highly complex nature of such liquors. A new lime liquor (unless it has been sharpened by the addition of sodium sulphide, carbonate, etc.) is, of course, merely a saturated solution of lime containing an excess of lime in suspension. As these liquors become old and "mellow" through continued use, there accumulates considerable quantities of ammonia, dissolved hide substance and its degradation products, etc., resulting largely through bacterial and enzyme action.

One of the most useful papers on the subject which have been published within recent years is that by Bennett,[1] who goes very thoroughly into analytical details. Many of the methods given below are taken from this paper.

Total Alkalinity.—Bennett suggests two methods for this determination, which includes alkalinity due to dissolved lime, amino acids and their calcium salts, sulphides and soda, if these two latter have been added.

(1) *Direct Method.*—50 c.cs. of the filtered liquor is pipetted into a 200 c.c. graduated flask containing a warm solution of 6 grms. of boric acid on 100 c.cs. of water. The boric acid precipitates the peptone matters which are the cause of the uncertain end point if the liquor is titrated direct. The flask and its contents are kept on the boiling water bath for a short time until the precipitate flocculates, and then cooled down under the tap and made up to the mark with distilled water. (Care must be taken to see that the boric acid used for the experiment is neutral to methyl orange.) After well mixing, the solution is filtered, for preference through a Whatman No. 5 filter paper, and 40 c.cs. of the filtrate, corresponding to 10 c.cs. of the original liquor, titrated with $\frac{N}{10}$ HCl, using methyl orange as indicator. This titration gives a measure of the total alkalinity of 10 c.cs. of the liquor.

(2) *Indirect Method.*—10 c.cs. of the filtered liquor is pipetted into a basin or flask containing 20 c.cs. of $\frac{N}{10}$ HCl. The mixture is diluted with a little distilled water and boiled for about 3 minutes to expel any H_2S. It is then cooled down and the excess of $\frac{N}{10}$ acid titrated back with $\frac{N}{10}$ NaOH, using methyl orange as indicator. The above methods give identical results.

The same author, in another communication,[2] gives a method for determining the "mellowness" of a lime liquor for control purposes. 25 c.cs. of the liquor is placed in a porcelain basin and phenol phthalein added. $\frac{N}{10}$ HCl is slowly run in until the pink colour disappears. This gives approximately the alkalinity due to strong bases. Methyl orange is now added, and the titration continued until the indicator just turns red. This last titration represents weak bases, such as amino compounds, etc., and, in regular systems of liming, will be proportional to the amount of dissolved hide substance. This method is of interest from the works' control point of view, as, by determining this titration difference and the total nitrogen in a few liquors from the same system, a factor for converting the former into the latter can be obtained. Some typical results quoted by Bennett to show this relationship are given below—

Methyl orange titration as above on 25 c.cs.	Total NH_3 by Kjeldahl equiv. to c.cs. $\frac{N}{10}$ NaOH	
4·10	2·8	0·68
5·37	3·5	0·68
11·00	7·45	0·68
11·75	8·05	0·68
13·50	9·05	0·67

Sulphides will influence the above factor, but in control work, the error will be a constant. The method is useful for rough work, but, of course, does not aim at extreme accuracy.

Ammonia.—The most accurate method for estimating free ammonia in lime liquors is that devised by Thompson and Suzuki,[3] which consists in distilling the ammonia into standard acid in vacuo. 25 c.cs. of the settled liquor is pipetted into the

distilling flask A (Fig. 2) fitted with a thermometer and a long fine capillary tube for admitting a small current of air to prevent frothing, etc. The liquor is diluted to about 200 c.cs. with distilled water, made slightly acid with dilute HCl, and then alkaline with an excess of magnesium oxide.

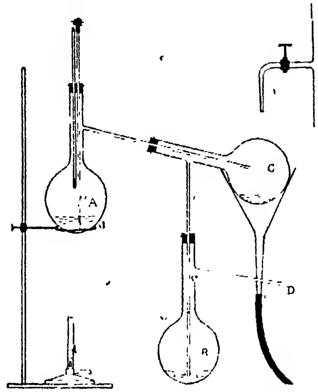

FIG. 2.—Thompson and Suzuki's apparatus.

The receiver (B) and the guard flask (C) each contain a known volume of $\frac{N}{10}H_2SO_4$, and care is taken to see that the side tube of the flask C dips well below the surface of the acid in B.

The apparatus is then exhausted by means of a pump connected to D, and the contents of the distilling flask distilled at a temperature of 40° C. for half an hour. During distillation, the guard flask C is kept cool by means of a stream of water as shown. After distillation, the excess of acid in flasks B and C is titrated back, using either methyl orange or carminic acid as indicator.

The following example will show the method of calculating results:—

25 c.cs. of settled liquor used.

	Flask B.	Flask C.
$\frac{N}{10}$ acid added	20·0 c.cs.	20·0 c.cs.
$\frac{N}{10}$ NaOH used in titrating back	18·4 c.cs.	17·0 c.cs.
$\frac{N}{10}$ acid used by NH_3	1·6 c.cs.	3·0 c.cs.

$\therefore$ Total $\frac{N}{10}$ acid used = 4·6 c.cs.

Now 1 c.c. of acid = 0·0017 gm. of NH_3

$\therefore$ 4·6 c.cs. of acid = (0·0017 × 4·6) gm. NH_3

= 0·00782 gm. NH_3

25 c.cs. of liquor contain 0·00782 gm. NH_3

100 c.cs. " " 0·03128 gm. NH_3.

Bennett points out that, in distilling ammonia from lime liquors under ordinary atmospheric pressure, it is necessary to fix a limit to the time of distillation. This is to avoid the gradual decomposition of the dissolved amino compounds with the production of further quantities of ammonia. The following method is recommended:—

100 c.cs. of the settled lime liquor is measured into a distillation flask together with 20 c.cs. of a 10 per cent. solution of magnesium sulphate and 75 c.cs. of water. (The magnesium sulphate renders the solution weakly alkaline with $Mg(OH)_2$.) The contents of the flask are now distilled into 50 c.cs. of a 3 per cent. solution of boric acid for exactly 15 minutes, at the end of which time the ammonia collected is titrated direct with $\frac{N}{10}$ HCl, using methyl orange as indicator.

$$1 \text{ c.c. } \frac{N}{10} \text{ acid} = 0·0017 \text{ gm. } NH_3$$

Sulphides.—The sulphide present in a lime liquor can be estimated volumetrically by the ammoniacal $\frac{N}{10}$ $ZnSO_4$ method as for ordinary sodium sulphide (see p. 16), using a known volume of the filtered or settled liquor. The accurate estimation of sulphides in lime liquors has been a matter of much controversy, and Bennett considers that the percentage error by the zinc sulphate method is very great. On the other hand, Hayes[4] favours the method as being quite suitable for ordinary purposes.

It appears from some recent work by Wood and Law[5] that sulphides are formed in lime liquors during the liming of hides, etc., by the action of the lime on the loosely combined sulphur in the hair. This is of interest, as it is therefore possible that sulphides can be detected in liquors to which no sulphide has been added.

Total Nitrogen.—50 or 100 c.cs. of the filtered liquor is rendered acid with an excess of dilute nitrogen free H_2SO_4 and evaporated to a small bulk in a Kjeldahl flask. The solution is then cooled down and 10 c.cs. of concentrated

sulphuric acid added. Digestion is continued in the ordinary manner, using towards the end of the operation 2–5 gms. of potassium sulphate and a small crystal of copper sulphate. When completely clear, and of a blue colour, the flask is cooled down and the contents diluted with distilled water. The solution is transferred to a distillation apparatus, rendered alkaline with an excess of caustic soda solution and the ammonia distilled into 50 c.cs. of a saturated boric acid solution, as described on p. 24. The ammonia is then titrated as usual.

$$1 \text{ c.c. } \frac{N}{10} \text{ acid} = 0{\cdot}0014 \text{ gm. N}$$

or, $$= 0{\cdot}0017 \text{ gm. } NH_3$$

The differentiation of the various nitrogenous compounds may be carried out by the method of Wood and Trotman.[6] A known volume of the clear liquor is heated with an excess of a saturated solution of zinc sulphate to precipitate the unchanged gelatine. The precipitate is filtered off, washed with a little water and its nitrogen content determinated by the Kjeldahl method. Gelatine may be taken to contain 18 per cent. of nitrogen.

To the filtrate from the above precipitation is added a slight excess of bromine water to precipitate the peptones. This precipitate is filtered off, washed, and the nitrogen determined. The quantity of nitrogen multiplied by the factor 5·42 will give the amount of peptone bodies present. Any nitrogen found in the filtrate represents amines and amino compounds.

For precipitating peptones, Trotman and Hackford recommend a solution of tannic acid.

Total Lime.—50 c.cs. of the clear liquor is evaporated to dryness in a platinum or porcelain basin, and ignited to destroy all organic matter. The residue is dissolved in dilute HCl and the solution boiled and filtered. The filtrate is made alkaline with an excess of ammonia (filtered if necessary) and the lime precipitated in the usual way with ammonium oxalate, washed, dried, ignited and weighed as already described (see p. 12).

Soda.—*Proctor's Method.*—50 c.cs. of the clear liquor is evaporated to dryness, ignited to destroy organic matter, and the residue, when cool, treated with a little ammonium carbonate solution. This is necessary, in order to convert all lime present into $CaCO_3$. The basin is again gently ignited to expel ammonia, and the residue washed on to a filter paper

with hot distilled water. The filtrate and washings are titrated with $\frac{N}{10}$ HCl using methyl orange as indicator.

$$1 \text{ c.c. } \frac{N}{10} \text{HCl} = 0{\cdot}0053 \text{ gm. } Na_2CO_3$$

Bennett's Method.—100 c.cs. of the filtered liquor is pipetted into a 200 c.c. graduated flask and 10 c.cs. of 10 per cent. ammonia added. The flask and its contents are heated on the water bath, and a hot solution, consisting of 20 c.cs. of saturated ammonium oxalate and 10 c.cs. of 10 per cent. ammonia added.

After further heating on the water bath for a quarter of an hour, the flask is cooled down under the tap, made up to the mark with water, well shaken and filtered.

50 c.cs. of the filtrate (equivalent to 25 c.cs. of the original liquor) is evaporated to dryness in a platinum basin, and the residue strongly ignited to drive off all ammonium salts. It is then dissolved in 25 c.cs. of warm 3 per cent. boric acid solution and the alkali titrated with $\frac{N}{10}$ HCl using methyl orange as indicator.

Any soda found by either of the above methods may be due to added soda or sodium sulphide or both.

In the routine examination of lime liquors it will be found most convenient to express all results in gms. per litre of liquor. Series of analyses are then easily tabulated for comparative purposes. Gm. per litre corresponds to lb. per 100 gallons.

Fellmonger's collecting limes.—The composition of fellmonger's collecting limes is the subject of a paper by Wood and Trotman.[7] The bad condition of these limes is said to be the cause of "looseness" in sheepskins. The results of analyses made by these authors are summarised below—

(Per 100 c.c. Liquor.)

	CaO in solution	Alkalinity N acid	NH_3	Total N.	Hide subs.
Min. . . .	0·03 gm.	3·88 c.cs.	0·008 gm.	0·023 gm.	0·129 gm.
Max. . . .	0·14 gm.	12·80 c.cs.	0·09 gm.	0·600 gm.	3·370 gm.
Mean . . .	0·083 gm.	6·50 c.cs.	0·033 gm.	0·105 gm.	1·043 gm.

They recommend that the following should be taken as the limits for a collecting lime :—

CaO in solution : Not less than 0·1 gm. per 100 c.cs.

Alkalinity : Not more than 6·0 c.cs. $\frac{N}{1}$ acid per 100 c.cs.

REFERENCES

[1] *Coll.* (London Edition), 1915, p. 258 *et seq.*
[2] *J.S.C.I.*, 1909, p. 292.
[3] *Jour. Soc. Leather Trades Chem.*, 1917, p. 140.
[4] *Ibid.*, 1918, p. 258.
[5] *J.S.C.I.*, 1916, p. 585.
[6] *Ibid.*, 1904, p. 1071.
[7] *Ibid.*, 1909, p. 1304.

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CHAPTER VI

ANALYSIS OF LIMED PELT

THE analysis of limed pelt has for its object the determination of the condition of the pelt after washing, and also the amount of acid required for deliming. (Although less than the theoretical quantity is generally used in practice.)

The methods of analysis as outlined by Bennett[1] have been found by the present author to give satisfactory results, and are described below.

Total Alkalinity.—10 gms. of the pelt is weighed out, and cut into very fine shavings on a clean glazed porcelain tile with a sharp knife. The pelt is then transferred to a wide-mouth glass-stoppered bottle, and the tile washed with distilled water, the washings being added to the bottle. 50 c.cs. of a 3 per cent. solution of boric acid is added to the bottle, the stopper of which is then tightly inserted and the whole shaken for a few hours, preferably in a mechanical shaker. The liquid is titrated with $\frac{N}{10}$ HCl, using methyl orange as indicator. The volume of acid required is noted, and the bottle and its contents again shaken for some hours. This process of shaking and subsequent titration is continued until the volume of acid required to be added is reduced to 0·1 c.c. The total amount of acid used in the titrations is ascertained by addition, and this gives a measure of the alkalinity of the pelt.

Such alkalinity is due to lime, soda, ammonia, and any sulphides and organic bases present, and is conveniently expressed as c.cs. $\frac{N}{10}$ acid per 100 gm. pelt.

Ammonia.—The small amount of ammonia present in limed pelt can be estimated in the neutralised liquid from the estimation of the total alkalinity above. This liquid is transferred to a distillation flask and diluted with distilled water. It is then made alkaline with an excess of caustic soda

solution, and any ammonia thus liberated is distilled over into about 50 c.cs. of a 3 per cent. boric acid solution. The ammonia is then titrated with $\frac{N}{10}$ acid in the usual way.

$$1 \text{ c.c. } \frac{N}{10} \text{ acid} = 0{\cdot}0017 \text{ gm. } NH_3$$

Sulphides.—According to Bennett, the sulphide present in limed pelt can be most accurately estimated by Mohr's residual method. For this process, the following standard solutions are required:—

(1) $\frac{N}{10}$ arsenite solution: This is prepared by weighing exactly 4·95 gms. of pure arsenious oxide As_2O_3 into a 1000 c.c. graduated flask and adding 200 c.cs. of water and 30 gms. of pure sodium bi-carbonate. The mixture is warmed on the water bath at 60 C. until the oxide has completely dissolved, when it is cooled down under the tap and made up to 1000 c.cs. with distilled water.

(2) $\frac{N}{10}$ iodine solution: 12·7 gms. of pure re-sublimed iodine is weighed into a 1000 c.c. graduated flask, 25 gms. of potassium iodide and 200 c.cs. of water added, and the mixture gently shaken until the iodine has dissolved. The solution is made up to 1000 c.cs. with distilled water.

1 c.c. of this solution should correspond to 1 c.c. of the arsenite solution when titrated against the latter, using starch paste as indicator.

(3) Approximately normal NaOH, made by dissolving 40 gms. of pure caustic soda in water and making the solution up to 1000 c.cs. with distilled water.

Method.—50 gms. of the pelt is weighed into a distillation flask and treated with 300 c.cs. of 10 per cent. HCl. The flask is then connected up to a distillation apparatus, the receiver of which contains 10 c.cs. of the approximately normal NaOH. After standing overnight, the solution in the distillation flask is warmed gently for half an hour, at the end of which time it is boiled for 20 minutes. The liquid in the receiver, now containing all H_2S evolved from the pelt, in the form of sodium sulphide, is transferred to a 200 c.c. graduated flask and 20 c.cs. of the $\frac{N}{10}$ arsenite solution added. The whole is then made slightly acid with dilute HCl. Arsenious sulphide is precipitated proportional

to the sulphuretted hydrogen present. In other words, some of the arsenite solution will be used up.

$$3H_2S + As_2O_3 = As_2S_3 + 3H_2O$$

The contents of the flask are made up to 200 c.cs. with water, well shaken and filtered. 100 c.cs. of the filtrate (= 25 gms. original pelt and 10 c.c. $\frac{N}{10}$ arsenite solution) is pipetted into a conical flask and rendered alkaline with an excess of sodium bi-carbonate. It is then titrated with $\frac{N}{10}$ iodine solution, using starch paste as indicator. The iodine solution required to titrate back represents the unused arsenite solution.

$$As_2O_3 + 4I_2 + 4H_2O = 8HI + 2As_2O_5$$

1 c.c. arsenite solution = 0·018018 gm. $Na_2S \cdot 9H_2O$
or = 0·00255 gm. H_2S

The following example will show the method of calculating the result:—

50 gms. pelt treated as above.
100 c.cs. of the filtrate used for titration.

Volume of arsenite solution in 100 c.cs. =	10·0 c.cs.
Iodine used for titrating back	7·5 c.cs.
Arsenite consumed by the sulphide	2·5 c.cs.

Now 1 c.c. arsenite = 0·018018 gm. $Na_2S \cdot 9H_2O$
∴ 2·5 c.cs. „ = 0·045045 gm. „ „
25 gms. pelt contain 0·045045 gm. „ „
100 gms. „ „ 0·18018 gm. „ „

Hide Substance.– The total hide substance in limed pelt is determined by estimating the total nitrogen by Kjeldahl's method (see p. 21).

5 gms. of the pelt is weighed into a Kjeldahl flask and digested with concentrated sulphuric acid in the usual way. The acid liquid is then diluted with water, cooled and made up to 500 c.cs. in a graduated flask. 100 c.cs. of this solution corresponding to 1 gm. of pelt is pipetted into a distillation flask, an excess of NaOH solution added and the ammonia estimated by distillation as previously described. Any nitrogen found in the form of free ammonia should be allowed for when calculating the hide substance.

Soda.—10 gms. of the pelt is gently ignited in a platinum dish, until all volatile matter has been expelled and only a

charred mass remains. This is carefully broken down with a glass rod, and the ignition completed to a white ash. It is then cooled and moistened with a solution of ammonium carbonate, and the excess driven off by careful ignition. This latter operation should be repeated in order to make sure that carbonation is complete.

The cooled residue is extracted with hot water several times and the washings filtered through a filter paper. The filtrate containing the sodium carbonate is then titrated with $\frac{N}{10}$ HCl, using methyl orange as indicator.

$$1 \text{ c.c. } \frac{N}{10} \text{ acid} = 0{\cdot}0053 \text{ gm. } Na_2CO_3$$

Total Lime.—The total lime can be estimated by igniting a known weight of pelt in a platinum dish and estimating the lime in the ash by the method described on p. 12.

Salt.—10 gms. of the pelt is gently ignited in a porcelain basin until only a charred mass remains. This is cooled down, moistened with distilled water and carefully crushed with a glass rod and extracted with boiling water several times, the washings being passed through a filter paper into a clean conical flask. One drop of a very dilute solution of methyl orange is added to the filtrate, which is then made exactly neutral by adding $\frac{N}{10}$ sulphuric acid. A few drops of potassium chromate solution is added, and the chlorine titrated with $\frac{N}{10}$ silver nitrate solution.

$$1 \text{ c.c. } \frac{N}{10} AgNO_3 = 0{\cdot}00585 \text{ gm. } NaCl$$

An alternative method for estimating chlorides is given by Bennett in the paper already referred to.

REFERENCE

[1] *Coll.* (London Edition), 1916, p. 85.

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CHAPTER VII

ANALYSIS OF LACTIC ACID

COMMERCIAL lactic acid, as used in the leather industry, is a light brown coloured liquid, containing, in addition to lactic acid, varying quantities of lactic anhydride, and acetic acid. Small quantities of iron may also be present, and sulphuric acid is known to have been used as an adulterant. The analysis of the commercial acid consists in the determination of the above constituents.

The solution for analysis is made by diluting 10 gms. of the sample to 250 c.cs. with distilled water.

Total Acidity.—25 c.cs of the diluted sample is measured into a conical flask, a few drops of phenol phthalein added and titrated with $\frac{N}{10}$ NaOH. This titration represents acidity due to lactic acid, acetic acid, and sulphuric acid if present. For the purposes of calculation, this titration is called A.

Acetic Acid.—25 c.cs. of the diluted solution is pipetted into a distillation flask and diluted to about 200 c.cs. with water. The volatile acid is then distilled over into a clean conical flask. A safety trap, similar to that used in the apparatus for the Kjeldahl ammonia distillation should be interposed between the distillation flask and the condenser. When about 100 c.cs. of distillate has been collected it is titrated with $\frac{N}{10}$ NaOH, using phenol phthalein as indicator. This titration represents the acetic acid from 25 c.cs. of the solution. If this titration be called B, then (A-B) will give the number of cubic centimetres of $\frac{N}{10}$ NaOH corresponding to the lactic acid (providing no sulphuric acid is present).

$$1 \text{ c.c. } \frac{N}{10} \text{NaOH} = 0{\cdot}009 \text{ gm. lactic acid, and}$$
$$= 0{\cdot}006 \text{ gm. acetic acid}$$

For other suggestions for estimating volatile acid, see publications by Faust,[1] Balderston.[2]

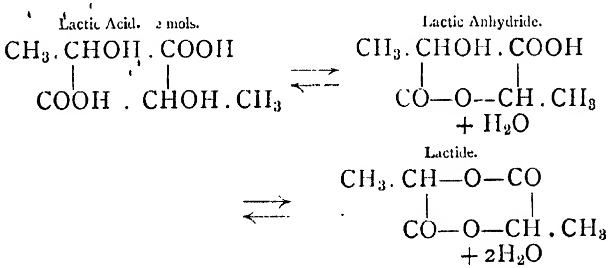
Lactic Anhydride.—25 c.cs. of the lactic acid solution is exactly neutralised by adding the necessary volume of $\frac{N}{10}$NaOH as found in the total acidity titration. An excess of 10 cubic centimetres of $\frac{N}{10}$NaOH is added, and the mixture allowed to stand in the cold for 10 minutes (Besson),[3] during which time the flask should be corked to prevent the absorption of atmospheric CO_2.

A few drops of phenol phthalein solution is added, and the excess of NaOH titrated back with $\frac{N}{10}$HCl.

In order to obtain uniform results, it is important that the anhydride determination should be made as soon as the sample is diluted. Lactide, which appears to be the actual substance present in lactic acid, is gradually transformed into lactic acid on diluting the sample (Thompson and Suzuki).[4]

$$1 \text{ c.c. } \frac{N}{10}\text{NaOH} = 0{\cdot}0072 \text{ gm. lactide}$$

The relation between lactic acid, lactic anhydride and lactide is shown below (Thompson and Suzuki, *loc. cit.*).



Total Ash and Iron.—5 gms. of the sample is ignited in a platinum dish and the residual ash weighed. For the determination of the iron, the ash is dissolved in a little nitric acid, and any iron present estimated colorimetrically by the method given under water analysis (see p. 2).

For light coloured samples, Harvey[5] recommends the following:—

25 c.cs. of the sample are diluted to 500 c.cs. in a graduated

flask, and 25 c.cs. of this solution measured into a Nessler glass and diluted to the 100 c.cs. mark with water.

1 c.c. of a 10 per cent. solution of potassium ferrocyanide is added, and the colour produced allowed to develop for 3 minutes. The tint is then matched against a standard iron solution with the usual precautions.

Sulphuric Acid.—Balderston (*loc. cit.*) recommends the following method :—

50 gms. of the sample is dissolved in neutral 95 per cent. alcohol, the solution heated to 60° C. and allowed to stand in a warm place overnight. Any precipitate is then filtered off and washed with alcohol. The alcohol is distilled off from the filtrate and the residue dissolved in a little dilute HCl. The solution is boiled, and any sulphuric acid precipitated by adding an excess of hot barium chloride solution. The barium sulphate is filtered off, washed with hot distilled water, dried, ignited and weighed.

$$BaSO_4 \text{ into } H_2SO_4 = 0{\cdot}420$$

This method depends upon the insolubility of sulphates and the solubility of sulphuric acid in alcohol.

Specific Gravity.—The specific gravity of the sample can be taken by means of the specific gravity bottle. This figure is useful as a check on different batches of the same delivery, and also as a means of converting percentages by weight into percentages by volume.

REFERENCES

[1] *Jour. Amer. Leather Chem. Assoc.*, 1915, p. 75.
[2] *Ibid.*, p. 242.
[3] *Coll.*, 1910, p. 73.
[4] *Jour. Soc. Leather Trades Chem.*, 1918, p. 115.
[5] *Ibid.*, p. 37.

NOTES

CHAPTER VIII

OTHER DELIMING AGENTS

In addition to lactic acid, many other acids are used for deliming, *e.g.* sulphuric acid, hydrochloric acid, acetic acid, formic acid, and boric acid. Ammonium chloride is also used. The examination of these materials is outlined below.

Sulphuric Acid.—For approximate work, the specific gravity is determined by means of a specific gravity bottle, or hydrometer, and from this figure the strength of the acid ascertained from the table (see Table I).

TABLE I.

SPECIFIC GRAVITY OF SULPHURIC ACID AT $\frac{15°}{4}$ C.

(Lunge).

S.G.	H_2SO_4	S.G.	H_2SO_4	S.G.	H_2SO_4	S.G.	H_2SO_4
1·200	27·32	1·305	39·77	1·410	51·15	1·515	61·12
1·205	27·95	1·310	40·35	1·415	51·66	1·520	61·59
1·210	28·58	1·315	40·93	1·420	52·15	1·525	62·06
1·215	29·21	1·320	41·50	1·425	52·63	1·530	62·53
1·220	29·84	1·325	42·08	1·430	53·11	1·535	63·00
1·225	30·48	1·330	42·66	1·435	53·59	1·540	63·43
1·230	31·11	1·335	43·20	1·440	54·07	1·545	63·85
1·235	31·70	1·340	43·74	1·445	54·55	1·550	64·26
1·240	32·28	1·345	44·28	1·450	55·03	1·555	64·67
1·245	32·86	1·350	44·82	1·455	55·50	1·560	65·20
1·250	33·43	1·355	45·35	1·460	55·97	1·565	65·65
1·255	34·00	1·360	45·88	1·465	56·43	1·570	66·09
1·260	34·57	1·365	46·41	1·470	56·90	1·575	66·53
1·265	35·14	1·370	46·94	1·475	57·37	1·580	66·95
1·270	35·71	1·375	47·47	1·480	57·83	1·585	67·40
1·275	36·29	1·380	48·00	1·485	58·28	1·590	67·83
1·280	36·87	1·385	48·53	1·490	58·74	1·595	68·26
1·285	37·45	1·390	49·06	1·495	59·22	1·600	68·70
1·290	38·03	1·395	49·59	1·500	59·70	1·605	69·13
1·295	38·61	1·400	50·11	1·505	60·18	1·610	69·56
1·300	39·19	1·405	50·63	1·510	60·65	1·615	70·00

TABLE I.—*Continued.*

S.G.	H_2SO_4.	S.G.	H_2SO_4.	S.G.	% H_2SO_4.	S.G.	% H_2SO_4.
1·620	70·42	1·710	78·04	1·800	86·92	1·834	93·25
1·625	70·85	1·715	78·48	1·805	87·60	1·835	93·56
1·630	71·27	1·720	78·92	1·810	88·30	1·836	93·80
1·635	71·70	1·725	79·36	1·815	89·05	1·837	94·20
1·640	72·12	1·730	79·80	1·820	90·05	1·838	94·60
1·645	72·55	1·735	80·24	1·821	90·20	1·839	95·00
1·650	72·96	1·740	80·68	1·822	90·40	1·840	95·60
1·655	73·40	1·745	81·12	1·823	90·60	1·8405	95·95
1·660	73·81	1·750	81·56	1·824	90·80	1·8410	96·30
1·665	74·24	1·755	82·00	1·825	91·00	1·8415	97·35
1·670	74·66	1·760	82·44	1·826	91·25	1·8410	98·20
1·675	75·08	1·765	83·01	1·827	91·50	1·8405	98·52
1·680	75·50	1·770	83·41	1·828	91·70	1·8400	98·72
1·685	75·86	1·775	84·02	1·829	91·90	1·8395	98·77
1·690	76·30	1·780	84·50	1·830	92·10	1·8390	99·12
1·695	76·73	1·785	85·10	1·831	92·43	1·8385	99·31
1·700	77·17	1·790	85·70	1·832	92·70		
1·705	77·60	1·795	86·30	1·833	92·97		

A more accurate method is to determine the acid by titration, 10 gms. of the sample is diluted with water and made up to 1000 c.cs. in a graduated flask. 25 c.cs. of the well mixed solution is titrated with $\frac{N}{10}$ NaOH or $\frac{N}{10}$ Na_2CO_3 with methyl orange as indicator.

$$1 \text{ c.c. } \frac{N}{10} \text{ alkali} = 0{\cdot}0049 \text{ gm. } H_2SO_4$$

The sample should also be examined qualitatively for iron, and, if necessary, estimated either by diluting the acid and precipitating with an excess of ammonia, or colorimetrically.

Hydrochloric Acid.—The specific gravity is determined, using a stoppered specific gravity bottle (HCl fumes are injurious to the balance). The strength of the acid can then be ascertained from Table II.

As a rule, the hydrochloric acid of commerce (spirits of salt) will be found to have a specific gravity of about 1·18, corresponding as will be seen from the table to a content of 35·5 per cent. HCl. The presence of sulphuric acid (which is unlikely) and sulphates can be ascertained by diluting a little of the sample and adding a solution of $BaCl_2$.

TABLE II.

SPECIFIC GRAVITY OF HYDROCHLORIC ACID AT 60°

(Ferguson).

S.G.	HCl	S.G.	HCl.	S.G.	HCl	S.G.	HCl.
1·0069	1·40	1·0985	19·63	1·1453	28·61	1·1789	35·21
1·0140	2·82	1·1006	20·04	1·1462	28·78	1·1798	35·40
1·0211	4·25	1·1027	20·45	1·1471	28·95	1·1808	35·59
1·0284	5·69	1·1048	20·86	1·1480	29·13	1·1817	35·78
1·0357	7·15	1·1069	21·27	1·1489	29·30	1·1827	35·97
1·0375	7·52	1·1090	21·68	1·1498	29·48	1·1836	36·16
1·0394	7·89	1·1111	22·09	1·1508	29·65	1·1846	36·35
1·0413	8·26	1·1132	22·50	1·1517	29·83	1·1856	36·54
1·0432	8·64	1·1154	22·92	1·1526	30·00	1·1866	36·73
1·0450	9·02	1·1176	23·33	1·1535	30·18	1·1875	36·93
1·0469	9·40	1·1197	23·75	1·1544	30·35	1·1885	37·14
1·0488	9·78	1·1219	24·16	1·1551	30·53	1·1895	37·36
1·0507	10·17	1·1240	24·57	1·1563	30·71	1·1904	37·58
1·0526	10·55	1·1248	24·73	1·1572	30·90	1·1914	37·80
1·0545	10·94	1·1256	24·90	1·1581	31·08	1·1924	38·03
1·0564	11·32	1·1265	25·06	1·1590	31·27	1·1934	38·26
1·0584	11·71	1·1274	25·23	1·1600	31·45	1·1944	38·49
1·0603	12·09	1·1283	25·39	1·1609	31·64	1·1953	38·72
1·0623	12·48	1·1292	25·56	1·1619	31·82	1·1963	38·95
1·0642	12·87	1·1301	25·72	1·1628	32·01	1·1973	39·18
1·0662	13·26	1·1310	25·89	1·1637	32·19	1·1982	39·41
1·0681	13·65	1·1319	26·05	1·1647	32·38	1·1993	39·64
1·0701	14·04	1·1328	26·22	1·1656	32·56	1·2003	39·86
1·0721	14·43	1·1336	26·39	1·1666	32·75	1·2013	40·09
1·0741	14·83	1·1345	26·56	1·1675	32·93	1·2023	40·32
1·0761	15·22	1·1354	26·73	1·1684	33·12	1·2033	40·55
1·0781	15·62	1·1363	26·90	1·1694	33·31	1·2043	40·78
1·0801	16·01	1·1372	27·07	1·1703	33·50	1·2053	41·01
1·0821	16·41	1·1381	27·24	1·1713	33·69	1.2063	41·24
1·0841	16·81	1·1390	27·41	1·1722	33·88	1·2073	41·48
1·0861	17·21	1·1399	27·58	1·1732	34·07	1·2083	41·72
1·0881	17·61	1·1408	27·75	1·1741	34·26	1·2093	41·99
1·0902	18·01	1·1417	27·92	1·1751	34·45	1·2103	42·20
1·0922	18·41	1·1426	28·09	1·1760	34·64	1·2114	42·64
1·0943	18·82	1·1435	28·26	1·1770	34·83	1·2124	43·01
1·0964	19·22	1·1444	28·44	1·1779	35·02	1·2134	43·40

For Titration.—10 gms. of the sample is diluted to 1000 c.cs. in a graduated flask, and 25 c.cs. of the solution titrated with $\frac{N}{10}$ NaOH with methyl orange as indicator.

$$1 \text{ c.c. of } \frac{N}{10} \text{NaOH} = 0{\cdot}00365 \text{ gm. HCl.}$$

Mineral Impurities.—20 gms. of the acid is evaporated to dryness on a water bath in a fume cupboard, and the residue greatly ignited. It is then weighed and examined for iron, etc.

Acetic Acid.—The strength of the acid can be arrived at by determining the specific gravity and referring to Table III.

TABLE III.

SPECIFIC GRAVITY OF ACETIC ACID AT 15° C.

(Oudemans).

S.G.	Acetic acid	S.G.	Acetic acid	S.G.	Acetic acid.	S.G.	Acetic acid.
0·9992	0	1·0363	26	1·0631	52	1·0748	78
1·0007	1	1·0375	27	1·0638	53	1·0748	79
1·0022	2	1·0388	28	1·0646	54	1·0748	80
1·0037	3	1·0400	29	1·0653	55	1·0747	81
1·0052	4	1·0412	30	1·0660	56	1·0746	82
1·0067	5	1·0421	31	1·0666	57	1·0744	83
1·0083	6	1·0430	32	1·0673	58	1·0742	84
1·0098	7	1·0447	33	1·0679	59	1·0739	85
1·0113	8	1·0459	34	1·0685	60	1·0736	86
1·0127	9	1·0470	35	1·0691	61	1·0731	87
1·0142	10	1·0481	36	1·0697	62	1·0720	88
1·0157	11	1·0492	37	1·0702	63	1·0720	89
1·0171	12	1·0502	38	1·0707	64	1·0713	90
1·0185	13	1·0513	39	1·0712	65	1·0705	91
1·0200	14	1·0523	40	1·0717	66	1·0696	92
1·0214	15	1·0533	41	1·0721	67	1·0686	93
1·0228	16	1·0543	42	1·0725	68	1·0674	94
1·0242	17	1·0552	43	1·0729	69	1·0660	95
1·0256	18	1·0562	44	1·0733	70	1·0644	96
1·0270	19	1·0571	45	1·0737	71	1·0625	97
1·0284	20	1·0580	46	1·0740	72	1·0604	98
1·0298	21	1·0589	47	1·0742	73	1·0580	99
1·0311	22	1·0598	48	1·0744	74	1·0553	100
1·0324	23	1·0607	49	1·0746	75		
1·0337	24	1·0615	50	1·0747	76		
1·0350	25	1·0623	51	1·0748	77		

10 gms. of the acid is diluted to 1000 c.cs. and 25 c.cs. of the solution titrated with $\frac{N}{10}$ NaOH, using phenol phthalein as indicator.

$$1 \text{ c.c. } \frac{N}{10} \text{ NaOH} = 0{\cdot}006 \text{ gm. acetic acid}$$

Formic Acid.—The sample is titrated as for acetic acid, above.

$$1 \text{ c.c. } \frac{N}{10} \text{ NaOH} = 0{\cdot}0046 \text{ gm. of formic acid}$$

For an alternative, and more accurate method, see *J.S.C.I.*, 1903, p. 1019.

Boric Acid.—This acid can only be satisfactorily titrated with an alkali in the presence of an excess of glycerol. 10 gms.

of the boric acid is dissolved in water and the solution made up to 1000 c.cs. in a graduated flask. 50 c.cs. of the solution is measured into a conical flask, made neutral to methyl-orange, and boiled to expel CO_2. After cooling quickly under the tap, 50 c.cs. of glycerine, previously made neutral to phenol phthalein, is added, and the mixture titrated with $\frac{N}{10}$ NaOH, using phenol phthalein as indicator.

$$1 \text{ c.c. } \frac{N}{10} NaOH = 0{\cdot}0062 \text{ gm. boric acid.}$$

Ammonium Chloride.—5 gms. of the sample is dissolved in water and the solution made up to 500 c.cs. in a graduated flask; 25 c.cs. are pipetted into a distillation flask (Fig. 1, p. 22) and diluted to about 200 c.cs. 20 c.cs. of a 10 per cent. solution of NaOH is added, and the ammonia liberated distilled into 50 c.cs. of a 3 per cent. boric acid solution. The ammonia is then titrated direct with $\frac{N}{10}$ HCl, using either Congo red or methyl orange as indicator.

$$1 \text{ c.c. } \frac{N}{10} HCl = 0{\cdot}00535 \text{ gm } NH_4Cl.$$

Non-Volatile Impurities.—5 gms. of the sample is ignited in a platinum dish in a fume cupboard. Ammonium chloride, being volatile, any residue left after ignition will be due to impurities. The residue is weighed and examined.

The Bran Drench.—A fermented infusion of bran is frequently used in the manufacture of light leathers for clearing the pucred skins and to complete deliming prior to tanning. Wood [1] has made an exhaustive study of this particular subject, and concludes that the carbohydrates are first hydrolysed to sugars by the enzyme cerealin, naturally present in the bran. The sugars are then fermented by B. Furfuris α and β (Wood) into organic acids.

Good bran has the following composition. Analyses made at the S.E. Agricultural College, Wye:—

	(1)	(2)
Moisture	14·20	12·04
Crude Protein	13·69	15·94
Oil	3·90	2·47
Ash	3·60	4·58
Crude Fibre	10·19	11·48
Carbohydrates	54·42	53·49
	100·00	100·00

The examination of bran is carried out on the following lines:—

Moisture.—5 gms. of the sample is dried at 105° C. until the loss in weight is constant. This loss is calculated as moisture. The dried residue from the moisture determination is ignited, and the ash weighed. The sand may be taken as that portion of the ash insoluble in dilute HCl.

Oil.—10 gms. of the bran is extracted with petroleum ether in a Soxhlet apparatus, as described on p. 72.

Crude Fibre.—The residue from the fat extraction is freed from the solvent by exposure to the air, and then boiled for exactly 30 minutes with 200 c.cs. of 1·25 per cent. sulphuric acid. The hot liquid is filtered through a clean piece of calico and the residue well washed with hot distilled water. It is then transferred to the beaker and boiled with exactly 200 c.cs. of 1·25 per cent. KOH solution for 30 minutes. It is then filtered through the calico filter and washed free from alkali with boiling water. The residue is put into a platinum dish and dried to constant weight in the steam oven and the weight noted. It is then ignited to a white ash and the loss on ignition taken as representing crude fibre.

Crude Proteins.—The nitrogen is estimated by the Kjeldahl method, using 2 gms. of the sample, and the percentage of nitrogen found is multiplied by the factor 6·25 to obtain the percentage of crude proteins.

Carbohydrates.—This figure is obtained by difference. The sum of the above determinations subtracted from 100 will give the percentage of carbohydrates, *i.e.* starch, sugars, etc.

The acids produced as the result of fermentation are formic, acetic, lactic, and a little butyric. Other substances formed are tri-methylamine, etc., and varying quantities of H, CO_2, H_2S, O, and N gases.

An examination of a drench liquor consists in the determination of volatile and non-volatile acidity.

Total Acidity.—50 c.cs. of the filtered drench liquor is titrated with $\frac{N}{10}$NaOH, using phenol phthalein as indicator.

Non-Volatile Acidity.—50 c.cs. of the liquor is evaporated in a porcelain basin on the water bath until it is reduced in volume to about 20 c.cs. The liquid is then cooled and titrated with $\frac{N}{10}$NaOH, using phenol phthalein as indicator. This titration gives the non-volatile acidity, and if subtracted from the total acidity will give that due to volatile acids.

The volatile acid is calculated as acetic acid, and the non-volatile acid as lactic acid.

$$1 \text{ c.c. } \frac{N}{10} NaOH = 0{\cdot}006 \text{ gm. acetic acid}$$

and

$$= 0{\cdot}009 \text{ gm. lactic acid}$$

For the complete separation of the different acids present in the drench liquor, the methods adopted by Wood (*loc. cit.*) can be used.

REFERENCE

[1] "Puering, Bating and Drenching of Skins" (Spon, 1912).

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CHAPTER IX

SINGLE BATH CHROME LIQUORS

SINGLE bath chrome liquors are largely prepared by reducing chromic acid with either an organic or an inorganic reducing agent. The chromic acid is first made by mixing a bichromate with an acid, and is afterwards reduced by adding the reducing agent. The following equation may be taken to represent the reaction which takes place when, say sulphuric acid and sodium bichromate is used :—

$$Na_2Cr_2O_7 + 3H_2SO_4 = 2CrSO_4(OH) + Na_2SO_4 + 3H_2O + 3O$$

The oxygen in the above equation is used up in the oxidation or the reducing substance. For reducing, the following can be used :—Glucose, cane sugar, glycerine, sawdust,[1] chrome leather scraps,[2] sodium bisulphite, sodium thiosulphate, and sulphur-di-oxide.[3] Using this latter substance, Balderston[4] suggests that the following reaction takes place :—

$$K_2Cr_2O_7 + 3SO_2 + H_2O = K_2SO_4 + Cr_2(OH)_2(SO_4)_2$$

Another method of preparing single bath chrome liquors is by rendering a chrome salt, *e.g.* chrome alum, chromium sulphate, etc., basic by the addition of an alkali such as washing soda.

$$Cr_2(SO_4)_3 + Na_2CO_3 + H_2O = Na_2SO_4 + CO_2 + 2CrSO_4(OH)$$

The theory of tanning by the single bath chrome process has been studied independently by Stiasny, Proctor and others, who conclude that the weak solution of basic chrome salt used, hydrolyses to give free acid, and a still more basic salt. The acid penetrates the hide fibre, and the basic salt is also absorbed, but at rates which vary with existing conditions. Blockey[5] has shown by electrometric methods that the acid is absorbed at a greater rate than the basic chrome salt.

A number of important papers relevant to the subject have been published recently, among which the following may be consulted with advantage :—

1. "The Adsorption of Chromic Oxide by Hide Powder." By A. W. Davison. *Jour. Amer. Leather Chem. Assoc.*, 1917, p. 258.

2. "The Action of Neutral Salts upon Chrome Tanning." By J. A. Wilson and E. J. Kern. *Jour. Amer. Leather Chem. Assoc.*, 1917, p. 445.

3. "Investigation of One Bath Chrome Liquors." By J. R. Blockey. *Jour. Soc. Leather Trades Chem.*, 1918, p. 205. Also M. E. Baldwin. *Jour. Amer. Leather Chem Assoc.*, 1919, p. 10.

4. "Acidity of Chrome Tanning Liquors." By A. W. Thomas and M. E. Baldwin. *Jour. Amer. Leather Chem. Assoc.*, 1918, p. 192.

5. "Action of Neutral Salts on Chrome Tanning Liquors." By A. W. Thomas and M. E. Baldwin. *Ibid.*, p. 248.

The examination of commercial chrome tanning liquors which average about 10 per cent. by volume of Cr_2O_3 can be carried by the methods given below.

With such liquors, the solution for analysis is prepared by diluting 20 c.cs. of the sample to 500 c.cs. in a graduated flask. 25 c.cs. of this solution is taken for the determinations, and the results obtained will correspond to 1 c.c. of the original sample. This method of dilution simplifies subsequent calculations.

Acidity.—25 c.cs. of the diluted solution is further diluted to about 50 c.cs. in a porcelain dish, and heated to the boil. A few drops of phenol phthalein solution is added, and the hot liquid titrated with $\frac{N}{10}$ NaOH until a faint reddish-violet colour is seen round the edge of the solution.

By this method, hydrolysis of the chrome salt takes place and the free sulphuric acid is neutralised by the NaOH.

$$CrSO_4(OH) + 2H_2O \rightleftharpoons Cr(OH)_3 + H_2SO_4$$
$$H_2SO_4 + 2NaOH = Na_2SO_4 + 2H_2O$$
$$1 \text{ c.c. } \frac{N}{10} NaOH = 0{\cdot}0048 \text{ gm. } SO_4$$

It will be noticed that sulphate present as sodium or potassium sulphate is not estimated by this method. It, therefore, gives a measure of the SO_4 present either in the free state or in combination with Cr. Iron and aluminium

salts adversely affects the titration, while Harvey[6] has shown that ammonium salts also affect the result, thus :—

$$(NH_4)_2SO_4 + 2NaOH = Na_2SO_4 + 2NH_3 + 2H_2O$$

If ammonium salts are present, the ammonia should be estimated by distillation, after making the liquid alkaline with NaOH, and the volume of $\frac{N}{10}$NaOH corresponding to the quantity of ammonia found deducted from the above titration before calculating the acidity.

Quite recently, there have appeared on the market concentrated chrome liquors made by reduction with SO_2, and it occasionally happens that an excess of the gas is present. In determining the acidity of such liquors, the titration should be commenced in the cold, and heated only after the indicator has turned red. Otherwise, by heating at the commencement, SO_2 may be expelled and a low acidity result will be obtained. After the indicator has turned red, the solution should be boiled, and the titration completed in the usual way.

Chromium.—Both volumetric and gravimetric methods can be used for the determination of the Cr.

Gravimetric Methods.—25 c.cs. of the diluted solution is pipetted into a beaker and diluted with about 100 c.cs. of water. The solution is then heated and a slight excess of ammonia added to precipitate the Cr in the form of $Cr(OH)_3$. After boiling for about 10 minutes the precipitate is filtered off through a pleated filter paper and thoroughly washed with hot distilled water. It is then dried, ignited in a tared crucible and weighed as Cr_2O_3. Alden[7] points out that the above method gives too high results, owing to the difficulty of washing the $Cr(OH)_3$ precipitate. This can be overcome to a large extent by re-dissolving the precipitate in HCl and re-precipitating with ammonia. If iron and (or) aluminium are present, they will be precipitated with the chromium. In such cases, the latter is more conveniently estimated volumetrically.

Another gravimetric method, proposed by Schœller and Schrauth,[8] is by the use of aniline. This reagent does not itself precipitate Cr, but combines with the acid produced by the hydrolysis of the chrome salt, with the result that the Cr is precipitated. The solution containing the Cr (0·1–0·2 gm.) is diluted to about 200 c.cs. and boiled. 3 c.cs. of aniline is then added in 1 c.c. portions, and the whole boiled for 5

minutes. The precipitate is filtered off, washed with hot distilled water, dried in the oven and then ignited and weighed as Cr_2O_3. (The vapour of aniline is extremely poisonous, and this operation should be conducted in a fume cupboard with a good draught arrangement.)

Volumetric Method.—Chromium in the form of chromic acid CrO_3 can be rapidly and accurately estimated by means of iodine and sodium thiosulphate.

25 c.cs. of the dilute solution is measured into a 500 c.c. Philip's beaker and diluted with an equal volume of water. The chromium is then oxidised to chromate by adding 1–2 gms. of sodium peroxide Na_2O_2 in small quantities at a time, or until the colour of the solution is yellow. The excess of peroxide is then decomposed by boiling the solution until effervescence ceases and the liquid boils steadily. If any precipitate of iron is observed, it should be filtered off at this stage. It has been pointed out by Lamb, Harvey[9] and others that iron interferes with the iodometric method of estimating Cr. The solution is cooled down, made acid with an excess of HCl, and again cooled if necessary. This converts the alkali chromate into chromic acid, thus

$$2Na_2CrO_4 + 4HCl = 2CrO_3 + 4NaCl + 2H_2O$$

An excess of potassium iodide solution is added, and the iodine liberated, titrated with $\frac{N}{10}$ sodium thiosulphate solution, using starch paste as indicator.

$$2CrO_3 + 6KI + 12HCl = 3I_2 + 2CrCl_3 + 6KCl + 6H_2O$$

$$I_2 + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6$$

$$1 \text{ c.c. } \frac{N}{10} Na_2S_2O_3 = 0{\cdot}00173 \text{ gm. Cr}$$

or

$$= 0{\cdot}00253 \text{ gm. } Cr_2O_3$$

The $\frac{N}{10}$ sodium thiosulphate is prepared by dissolving 24·82 gms. of the pure salt in water, and making the solution up to 1000 c.cs. in a graduated flask. This is standardised against either iodine or potassium bichromate.

Instead or sodium peroxide, potassium permanganate may be used for oxidising the chromium.

The solution containing the chromium is made alkaline with caustic soda, boiled, and a very slight excess of potassium permanganate solution added. The pink colour of the solution is then destroyed by adding a few drops of alcohol, after which the chromate is estimated as above, after filtering.

Smith and Enna[10] and McCandlish[11] point out the difficulty of oxidising the chromium in the presence of an excess of organic matter, such as, for example, in the case of used liquors. To overcome this, the chromium is first precipitated with ammonia, filtered off, and re-dissolved in dilute HCl. The chromium in the solution is then oxidised and estimated in the usual way.

In some cases when adding HCl to the alkaline chromate solution, the latter will turn an olive green colour instead of a deep orange red. This is a sure indication of the presence of organic matter, and if such is found to be the case, the method of Smith and Enna should be adopted, or more peroxide used for the oxidation. Liquors containing an excess of glucose are known to behave as above.

Basicity.—The basicity of a single bath chrome liquor is, in England, expressed as the number of parts of SO_4 combined with 52 parts of Cr. It has been found that the basic salt $CrSO_4(OH)$ is that most suitable for tanning. The basicity of a liquor containing the above salt would be therefore 96.

$$\underset{52}{Cr}\,\underset{96}{SO_4}\,\underset{17}{(OH)}$$

The basicity of a liquor is—

$$\frac{\%\ SO_4}{\%\ Cr_2} \times 52$$

The basicity of a liquor can be regulated by adding acid if too low, and alkali if too high. The following examples will show the method of calculation :—

Example 1.—A liquor has the following composition :—

Cr	10·0 per cent. by vol.
Acidity as SO_4 .	14·42 „ „
Basicity . . .	75

and it is required to raise the basicity to 90.

Basicity = SO_4 combined with 52 Cr.

$\therefore$ 52 Cr has $(90 - 75)$ SO_4 too little.

$= 15$

If 52 gms. of Cr have deficiency of 15 SO_4, 10 gms. (= 100 c.cs. of liquor) have a deficiency of—

$$\frac{15 \times 10}{52} = 3 \text{ approx.}$$

$\therefore$ every 100 c.cs. of the liquor requires 3 gms. of SO_4.

$$96\ SO_4 = 98 \text{ of } H_2SO_4$$
$$\therefore 3\ SO_4 = \frac{98 \times 3}{96}$$
$$= 3{\cdot}06 \text{ gms. } H_2SO_4$$

100 c.cs. of the liquor therefore requires 3·06 gms. of sulphuric acid to raise the basicity to 90.

Now, gms. per 100 c.cs. correspond to lb. per 10 gallons.

$\therefore$ 10 gallons will require 3·06 lbs. of sulphuric acid.

Example 2.—The liquor examined contains—

Cr	8·0 gms. per 100 c.cs.
Acidity as SO_4 .	16·3 gms. „ „
Basicity . . .	106

It is required to bring down the basicity to 96.

Now basicity = SO_4 combined with 52 Cr

$\therefore$ 52 Cr have (106 − 96) too much SO_4

and 8·0 gms. Cr (= 100 c.cs. of liquor) have $\frac{10 \times 8}{52}$

$$= 1{\cdot}58 \text{ gms. approx.}$$

$\therefore$ every 100 c.cs. of liquor has 1·58 gms. of SO_4 to be neutralised

$$\text{Now } 96\ SO_4 = 80\ NaOH$$
$$\text{and } 1{\cdot}58 \text{ gms.} = \frac{80}{96} \times 1{\cdot}58$$
$$= 1{\cdot}317 \text{ gms. } NaOH$$

100 c.cs. of liquor require 1·317 gms. of HaOH to bring the basicity to 96. This corresponds to 1·317 lbs. per 10 gallons.

Various other methods of expressing the basicity have from time to time been suggested, the most interesting and useful of which seems to be that by Blockey.[12] This is based on the number of (OH) groups attached to Cr_2. The author also gives a graph showing the relation between the results obtained by these various methods. This is given here for reference.

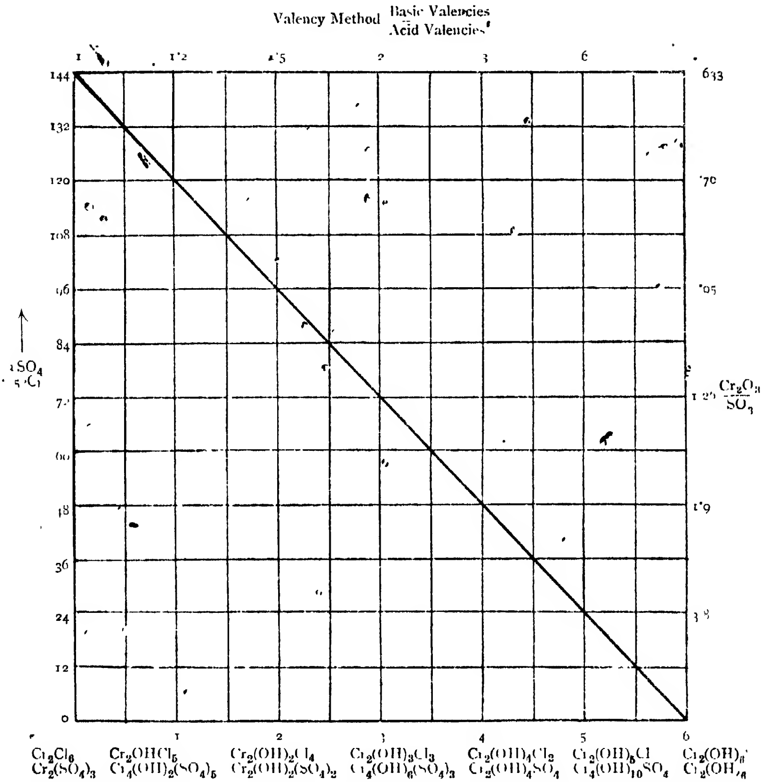

FIG. 3.—Blockey's Curve showing relations between the various methods of expressing basicity.

REFERENCES.

[1] Eng. Pat., 120,049, 1918. *Leather World*, 1919, p. 119.
[2] Ger. Pat., 295,518, 1914. *Coll.* (London Edition), 1917, p. 45.
[3] *Jour. Amer. Leather Chem. Assoc.*, 1917, p. 665.
[4] *Jour. Soc. Leather Trades Chem.*, 1919, p. 37.
[5] *Ibid.*, 1918, p. 209.
[6] *Ibid.*, 1918, p. 215.
[7] *Jour. Amer. Leather Chem. Assoc.*, 1916, p. 174.
[8] *Chem. Zeit.*, 1909, p. 1237.
[9] *Coll.* (London Edition), 1916, p. 201.
[10] *Jour. Soc. Leather Trades Chem.*, 1918, p. 213.
[11] *Jour. Amer. Leather Chem. Assoc.*, 1917, p. 440.
[12] *Jour. Soc. Leather Trades Chem.*, 1919, p. 11.

NOTES

CHAPTER X

TWO-BATH CHROME TANNING

CHROME tanning by the two-bath process involves, as the name suggests, the use of two distinct liquors. Hence, in the analytical control of the process, an examination of both liquors becomes necessary.

First Bath.—In the first instance, the possible composition of the first bath will be considered.

The first bath is a chromic acid liquor made by adding a mineral acid to a solution of a bichromate whereby chromic acid is formed.

$$Na_2Cr_2O_7 + H_2SO_4 = Na_2SO_4 + H_2O + 2CrO_3$$

or

$$K_2Cr_2O_7 + 2HCl = 2KCl + H_2O + 2CrO_3$$

Previous to the war, potassium bichromate was invariably used for this purpose, but owing to the scarcity and high price of this material, sodium bichromate has since been used with equal success. In using this salt, it must be remembered that the molecule contains two molecules of water of crystallisation, which must be allowed for in certain calculations.

It will be seen that a mixture of a bichromate and an acid may contain—

(*a*) Bichromate and chromic acid;

(*b*) Chromic acid and free mineral acid;

(*c*) Chromic acid only,

according to the relative quantities of acid and bichromate employed.

The analytical determinations necessary in order to establish the composition of first bath liquors are, acidity and total chromium. When examining liquors of the concentration commonly used for actual tanning, there will be no need to further dilute the sample.

Acidity.—25 c.cs. of the liquor is pipetted into a conical flask, and a few drops of phenol phthalein added. The liquid

is then titrated with $\frac{N}{10}$ NaOH until a permanent red colour is obtained. It may be necessary to add a little more of the indicator towards the end of the titration owing to the oxidising action of the chromic acid.

This acidity will, in addition to the chromic acid, include any free mineral acid and any bichromate. The latter reacts as an acid towards alkali and phenol phthalein by virtue of the half combined chromic acid present.

$$\underbrace{K_2CrO_4 . CrO_3}_{K_2Cr_2O_7} + 2NaOH = K_2CrO_4 + Na_2CrO_4 + H_2O$$

Chromium.—25 c.cs. of the liquor is measured into a conical flask and 1–2 c.cs. of concentrated HCl added. An excess of potassium iodide solution is then added and the liberated iodine titrated with $\frac{N}{10}$ $Na_2S_2O_3$, using starch paste as indicator.

Calculation of results.—Knowing the acidity of the liquor in terms of $\frac{N}{10}$ NaOH, and the $\frac{N}{10}$ $Na_2S_2O_3$ equivalent of the chromium, it is possible to calculate the composition of the liquor by means of the table given below, which was first worked out and published by Proctor.

TABLE IV.

(*Proctor.*)

Present	Prop $\dfrac{a \text{ c.cs. } \frac{N}{10} \text{ Hypo}}{b \text{ c.cs. } \frac{N}{10} \text{ NaOH}}$	Then—
Chromate only	$b = 0$	$K_2CrO_4 = a \times \cdot0065$
Bichromate only . . .	$a = 3b$	$K_2Cr_2O_7 = a \times \cdot0049$
Chromic acid only . . .	$a = \frac{3b}{2}$	$CrO_3 = b \times \cdot005$ or, $a \times \cdot0033$
Chromate and bichromate .	$a > 3b$	$K_2CrO_4 = (a - 3b) \times \cdot0065$ $K_2Cr_2O_7 = b \times \cdot0147$
Bichromate and chromic acid	$\frac{3b}{2} < a < 3b$	$K_2Cr_2O_7 = (2a - 3b) \times \cdot0049$ $CrO_3 = (3b - a) \times \cdot0033$
Chromic acid and HCl . .	$a < \frac{3b}{2}$	$CrO_3 = a \times \cdot0033$ $HCl = \left(b - \frac{2a}{3}\right) \times \cdot00365$ or, $H_2SO_4 = \left(b - \frac{2a}{3}\right) \times \cdot0049$

As examples of the calculations involved the following are given.

Example 1.—25 c.cs. of the liquor gave the following titrations:—

$$\frac{N}{10} Na_2S_2O_3 = 13{\cdot}7 \text{ c.cs.}$$
$$\frac{N}{10} NaOH = 9{\cdot}2 \text{ c.cs.}$$

Now, in the table given a = the thiosulphate reading, and b = the NaOH reading. The titrations correspond, within the limits of experimental error, to the formula $a = \frac{3b}{2}$.

Thus—

$$13{\cdot}7 = \frac{3 \times 9{\cdot}2}{2}$$

From this, it is evident that chromic acid only is present.

Therefore, 1 c.c. of $Na_2S_2O_3 = 0{\cdot}0033$ CrO_3
$13{\cdot}7$ c.cs. $Na_2S_2O_3 = (13{\cdot}7 \times 0{\cdot}0033)$ gm. CrO_3
$= 0{\cdot}04521$ gm. CrO_3 in 25 c.cs.
100 c.cs. of the liquor contain $0{\cdot}18084$ gm. CrO_3

Example 2.—25 c.cs. of the liquor gave the following results on titration:—

$$\frac{N}{10} Na_2S_2O_3 = 6{\cdot}8 \text{ c.cs.}$$
$$\frac{N}{10} NaOH = 5{\cdot}0 \text{ c.cs.}$$

By trial it is found that these values can be substituted in the formula coresponding to "free HCl and chromic acid." Thus—

$$a < \frac{3b}{2}$$
$$6{\cdot}8 \text{ is less than } \frac{3 \times 5{\cdot}0}{2}$$
$$6{\cdot}8 \text{ is less than } 7{\cdot}5$$

To calculate the quantities of free acid and chromic acid, the following formulæ must be used:—

$CrO_3 = (a \times 0{\cdot}0033)$
$= (6{\cdot}8 \times 0{\cdot}0033)$
$= 0{\cdot}02244$ gm. CrO_3 in 25 c.cs. of the liquor

$$\text{free acid} = \left(b - \frac{2a}{3}\right) \times 0{\cdot}0049\ H_2SO_4$$
$$= (5{\cdot}0 - 4{\cdot}5) \times 0{\cdot}0049\ H_2SO_4$$
$$= 0{\cdot}5 \times 0{\cdot}0049$$
$$= 0{\cdot}00245 \text{ gm. } H_2SO_4 \text{ in 25 c.cs. of the liquor.}$$

The Second Bath Liquor.—The second bath of the two-bath chrome tanning process consists of a solution of sodium thiosulphate made acid with HCl, which brings about the reduction of the chromic acid in the pelt. In the case of spent or once used liquors, any power of reduction can be measured by titrating a known volume with $\frac{N}{10}$ iodine solution with starch paste as indicator. This titration will include SO_2 and $Na_2S_2O_3$.

Examination of Commercial Hypo (Sodium Thiosulphate).—There are many methods which may be used for the analysis of sodium thiosulphate (hypo), of which the following are given as being rapid and convenient :—

(1) 20 gms. of the sample are dissolved in water and the solution made up to 1000 c.cs. in a graduated flask with distilled water.

25 c.cs. of this solution is pipetted into a conical flask, and a few drops of freshly made cold starch paste added. It is then titrated with $\frac{N}{10}$ iodine solution in the usual way.

$$1 \text{ c.c. } \frac{N}{10} \text{ iodine} = 0{\cdot}0248 \text{ gm. } Na_2S_2O_3 5H_2O$$

(2) An exactly decinormal solution of potassium bichromate is prepared by dissolving 4·913 gms. of the pure fused salt in water, and making the solution up to 1000 c.cs. in a graduated flask.

20 gms. of the sample of hypo is dissolved in water and made up to 1000 c.cs. 25 c.cs. of the bichromate solution is pipetted into a 500 c.c. conical flask, made acid with 5–6 c.cs. of concentrated HCl, and then 20 c.cs. of a 10 per cent. KI solution added. The liberated iodine is titrated with the hypo solution until the blue colour, produced by adding a few drops of starch paste when the liquor is a straw-yellow colour, is destroyed.

The bichromate solution, being $\frac{N}{10}$, 1 c.c. will correspond to 0·0248 gm. of pure thiosulphate, so that the 25 c.cs. used in the above test will = 0·62 gm.

This is, therefore, the amount of pure thiosulphate in the volume of the solution used in titration, from which the percentage of thiosulphate in the sample can be calculated.

(3) A more complete method, stated by Dr. Levi[1] to be that used by the Grasselli Chemical Co., U.S.A., is as follows:—

12 gms. of the sample is dissolved in water and made up to 1000 c.cs. 100 c.cs. of this solution is titrated with $\frac{N}{10}$ HCl, using methyl orange as indicator. This titration gives the $Na_2SO_3, 7H_2O$.

$$1 \text{ c.c. } \frac{N}{10} HCl = 0{\cdot}0252\ Na_2SO_3, 7H_2O$$

$$Na_2SO_3 + HCl = NaHSO_3 + NaCl$$

The neutral solution is then titrated with $\frac{N}{10}$ iodine solution, using starch paste as indicator. The volume of iodine is noted, and the blue colour of the solution destroyed by adding one drop of $\frac{N}{10} Na_2S_2O_3$. The acidity of the solution is then determined by titrating with $\frac{N}{10}$ NaOH.

$$NaHSO_3 + 2I + H_2O = NaHSO_4 + 2HI$$
$$2Na_2S_2O_3 + 2I = 2NaI + Na_2S_4O_6$$
$$NaHSO_4 + 2HI + 3NaOH = Na_2SO_4 + 2NaI + 3H_2O$$

Two-thirds of the NaOH reading is deducted from the iodine reading, and the difference multiplied by the factor 0·0248 will give the $Na_2S_2O_3, 5H_2O$.

One-third of the NaOH titration, less the HCl titration, gives $NaHSO_3$, factor = 0·0104.

For the estimation of sulphate, 5 gms. of the sample is dissolved in water and 10 gms. of Rochelle salt added. The solution is allowed to stand overnight and the sulphur filtered off. The sulphate in the filtrate is precipitated in the cold solution by adding $BaCl_2$. After standing for several hours, the $BaSO_4$ is filtered off, washed with very dilute HCl and then water. It is dried in the oven, ignited and weighed.

$$BaSO_4 \text{ into } Na_2SO_4 \cdot 10H_2O = 1{\cdot}38$$

A method of titrating thiosulphate without the use of iodine has been proposed by Besson.[2]

25 gms. of the sample is dissolved in water and the solution made up to 1000 c.cs. in a graduated flask. 10 c.cs. of this solution is pipetted into a flask, and treated with exactly 25 c.cs. of $\frac{N}{10}$ NaOH, and 20 c.cs. of neutral hydrogen peroxide. The mixture is heated on the water bath for 10 minutes and then cooled down. The excess of NaOH is titrated back with $\frac{N}{10}$ HCl, using methyl orange as indicator.

$$4H_2O_2 + Na_2S_2O_3 + 2NaOH = 2Na_2SO_4 + 5H_2O$$

$$1 \text{ c.c. } \frac{N}{10} NaOH = 0{\cdot}0124 \text{ gm. } Na_2S_2O_3, 5H_2O$$

The results obtained by Besson's method are slightly lower than those obtained by simple titration with iodine.

REFERENCES

[1] *Jour. Amer. Leather Chem. Assoc.*, 1907, p. 126.
[2] *Coll.*, 1907, pp. 193, 259.

LEATHER CHEMISTRY

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CHAPTER XI

COMMERCIAL EGG YOLK

EGG YOLKS are used in the leather trade in connection with the manufacture of glove leathers, and also as a constituent of fat-liquors, where they act as an emulsifier for the other oils used. The constituent of most importance is the fat, on the percentage of which the sample is usually valued. Allen gives the following detailed analysis of liquid egg yolk:—

Vitellin	15·8 per cent.
Nuclein . . .	1·5 ,,
Cerebrin	0·3 ,,
Lecithin	7·2 ,,
Glycero phosphoric acid	1·2 ,,
Cholesterin	0·4 ,,
Fats	20·3 ,,
Colouring matter . . .	0·5 ,,
Salts	1·0 ,,
Water	51·8 ,,

Many samples examined by the author have contained more than 20 per cent. of fat, as the following typical analysis shows:—

Moisture	48·3 per cent.
Oil	27·9 ,,
Mineral ash	1·9 ,,

The determinations usually made in the examination of a sample of egg yolk are moisture, oil, ash, and the nature and amount of preservative present.

Moisture.—About 10 gms. of clean dry sand and a short piece of glass rod are put into a clean flat-bottomed glass dish, and the whole dried in the steam oven for three hours and weighed. A quantity of the well-mixed sample (about 5 gms.) is added to the dish, which is then re-weighed. The whole is carefully mixed and dried in the steam oven, or a

hot-air oven at 102° C. if the temperature can be regulated, until there is no further loss on subsequent drying. The loss sustained on drying represents moisture.

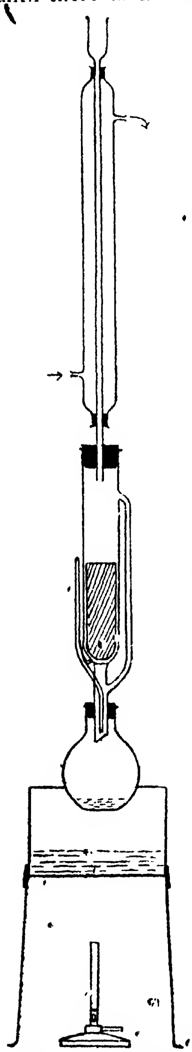

FIG. 4.—Extraction apparatus.

An example of the calculation is given below—

(1) Weight of basin, sand and rod only .	= 30·257 gms.
(2) Basin, sand, rod and yolk	= 35·721 „
(3) Weight of egg yolk added	= 5·464 „
(4) Weight of basin and contents	= 35·721 „
(4) Weight after heating to constant weight .	= 33·084 „
(5) Loss on heating . .	= 2·637 „

$$\text{Percentage of moisture} = \frac{100 \times 2{\cdot}637}{5{\cdot}464}$$
= 48·2 per cent. moisture.

NOTE.—In the above method it is very important to stir the contents of the basin frequently during the first hour of drying, otherwise the mass will cake together and be difficult to detach for the subsequent estimation of the fat. In addition to this, complete drying is rendered difficult and prolonged.

Oil or Fat.—The residue from the moisture determination, is carefully transferred to a small mortar and powdered. If necessary, the last traces of fat can be removed from the side of the dish by means of a piece of fat-free cotton wool. This is extracted later on with the yolk. The powdered yolk is now transferred to an extraction thimble and the pestle and mortar used wiped out with the same piece of cotton already used. This is then added to the thimble, being placed lightly over the surface of the dried yolk and sand, together with a little more fat-

free cotton wool. The thimble is put into a Soxhlet apparatus (Fig. 4) to which is attached a clean, dried, weighed flask. The yolk is then extracted with dry, light petroleum ether for 6 hours. The flask containing the solvent, in which will be dissolved all the fat, is removed from the Soxhlet and the petroleum ether distilled off. The residue consisting of the fat is then dried in a steam oven until constant in weight. The calculations necessary in order to arrive at the percentage of oil are—

Weight of yolk employed	=	5·464 gms.
Weight of flask + fat . .	=	27·382 „
„ „	=	25·861 „
Weight of fat	=	1·521 „

Percentage of fat . . . $= \dfrac{1{\cdot}521 \times 100}{5{\cdot}464}$

= 27·8 per cent. of fat.

If the sample has been preserved with boric acid, a small quantity will be extracted and weighed with the fat. When such is the case, the boric acid so extracted can be estimated as follows:—

The fat obtained from the above extraction is dissolved in a small volume of petrol ether and the solution extracted in a separating funnel with three or four successive quantities of water. For preference, the water used for the extractions should be slightly warm. The washings are united and treated with one-third their volume of glycerol. The solution is then titrated with $\frac{N}{10}$ NaOH, using phenol phthalein as indicated.

$$1 \text{ c.c. } \frac{N}{10} \text{ NaOH} = 0{\cdot}0062 \text{ gm. boric acid.}$$

The amount found is deducted from the weight of the extracted fat before calculating the percentage of the latter.

Another method for estimating the fat, proposed by Lamb and Harvey,[1] is as follows:—

A small quantity of the yolk is weighed in a beaker together with a glass rod. By means of this latter, the yolk is "spotted" on to an Adam's paper, or a clean strip of filter paper. The amount so "spotted" is ascertained by weighing the beaker and rod again. The paper is allowed to dry at room temperature, when it is extracted with petrol ether in the Soxhlet apparatus in the usual way.

According to these authors, the process is very convenient when examining a large number of samples. The following comparative figures were obtained :—

Sand Method.	Adam's Method.
27·7 per cent.	27·8 per cent.
22·00 "	21·90 "
11·09 "	11·11 "
24·63 "	24·76 "
23·20 "	23·11 "
26·81 "	26·73 "

Jean[2] finds that different solvents extract different amounts of "fatty matter," as shown in the following set of figures :—

Petroleum ether . . .	48·24 per cent.
Carbon disulphide . .	50·48 "
Ethyl ether	50·83 "
Carbon tetrachloride .	50·30 "
Chloroform	57·66 "

These differences are due to the solubility of lecithin, etc., in the various solvents. It is advisable, therefore, to always use petroleum ether for the fat extraction. Work on this particular point has also been carried out by Parker and Paul.[3]

Total Ash.—Two or three grams of the sample is ignited in a platinum dish until all organic matter has been driven off. The carbonaceous residue is broken up carefully with a rod, and extracted with water. The aqueous solution is decanted into a clean beaker and the residue dried and ignited to a pure white ash. The residue is cooled down and the washings obtained above added. The liquid is evaporated to dryness in the basin and the residue gently ignited. The total ash is then weighed. The extraction of the water soluble matter before complete ignition is necessary in order to avoid any loss of chlorides by volatilisation. If the ash exceeds 2 per cent., the yolk is, in all probability, preserved with common salt. In such cases, as much as 10–14 per cent. of ash may be found.

Salt.—The ash is dissolved in hot water and the solution cooled down and made up to a definite volume in a graduated flask. An aliquot part of this solution is measured into a flask, a few drops of potassium chromate added, and the chlorides titrated with $\frac{N}{10}$ silver nitrate.

$$1 \text{ c.c. } \frac{N}{10} AgNO_3 = 0{\cdot}00585 \text{ gm. NaCl.}$$

The salt can also be estimated in the residue from the fat extraction. This is transferred from the extraction thimble to a clean beaker and extracted with cold water. The aqueous solution is filtered and made up to a known volume. An aliquot part of this is taken and titrated with silver nitrate solution in the usual manner.

Boric.—The presence of boric acid can be ascertained by the following qualitative test. A few grams of the sample are ashed in the manner already described and then treated with a few drops of sulphuric acid and about 15 c.cs. of alcohol. The solution is then heated and the vapour of the alcohol ignited. In the presence of boric acid, the alcohol flame will be tinged green. For the quantitative estimation, the following modification of Thompson's method for the estimation of boric acid in milk can be used :—

10 gms. of the yolk is treated with 20 c.cs. of a 10 per cent. NaOH solution, and the whole evaporated to dryness on the water bath and ignited. The residue is boiled with 20 c.cs. of water and dilute HCl added until all but the carbon has dissolved. The solution is transferred to a 100 c.c. graduated flask and 0·5 gm. of $CaCl_2$ added. The solution is made just alkaline to phenol phthalein with caustic soda solution, after which 25 c.cs. of clear lime water is added. The whole is then made up to the 100 c.c. mark, well mixed and filtered.

50 c.cs. of the filtrate (= 5 gms. of the original yolk) is measured into a conical flask, a few drops of phenol phthalein added and titrated with $\frac{N}{1}$ H_2SO_4 until neutral, after which, methyl orange is added and the addition of acid continued until the yellow colour of the solution turns faintly pink. $\frac{N}{5}$ NaOH is then carefully added until the liquid just turns yellow. The liquid is boiled for a few minutes to expel any CO_2 and then cooled down. One-third of its volume of neutral glycerol is added, and titrated with $\frac{N}{10}$ NaOH until a permanent pink colour is produced.

$$1 \text{ c.c. } \frac{N}{10} \text{ NaOH} = 0{\cdot}0062 \text{ gm. boric acid.}$$

Proteins.—The nitrogen is estimated by the Kjeldahl

method, and the percentage found is multiplied by the factor 6·25 to obtain the proteins.

REFERENCES

[1] *Jour. Soc. Leather Trades Chem.*, 1917, p. 186.
[2] *Coll.*, 1903, p. 71.
[3] *Jour. Amer. Leather Chem. Assoc.*, 1910, p. 217.

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CHAPTER XII

SOAP ANALYSIS

BOTH hard and soft soaps are used in the leather industry. The former are the sodium salts, and the latter the potash salts of the fatty acids. Although this distinction is made, one frequently finds soft soaps containing no potash. These are generally made from castor oil, the soda salts of the fatty acids of which make a very good non-potassic soft soap. For general analytical purposes, the alkalies in hard soap are calculated as Na_2CO_3, $NaOH$, etc., and in soft soap as K_2CO_3, KOH, etc.

Soaps rapidly dry on exposure to air, so that it is necessary to conduct the analysis immediately on receipt of the sample. Soft soaps should be well mixed, and an average sample transferred to a wide-mouth glass stoppered bottle. In the case of hard soap, the end portions of the bar should not be taken for the analysis.

Fatty and Rosin Acids.—10 gms. of the sample is dissolved in 200 c.cs. of hot water, and exactly 50 c.cs. of normal H_2SO_4 added. The beaker containing the liquid is heated in the water bath until a clear oily layer of fatty and rosin acids separates out. A pleated filter paper and weighing bottle are dried in the steam oven and weighed. The paper is then made thoroughly wet with boiling distilled water and the fatty acids filtered. These will remain on the filter paper, while the aqueous liquid containing the excess of sulphuric acid will pass through quite clear. The fatty acids are well washed with hot distilled water until the washings no longer react acid to litmus paper. The paper and fatty acids are carefully transferred to the weighing bottle and dried in the steam oven until approximately constant in weight.

Total Alkali.—The filtrate from the determination of the total fatty acids is cooled, a few drops of methyl orange

added, and the excess of sulphuric acid titrated back with normal NaOH.

$$1 \text{ c.c. normal } H_2SO_4 = 0{\cdot}031 \text{ gm. } Na_2O$$
or
$$= 0{\cdot}047 \text{ gm. } K_2O$$

The following are examples of the calculations involved:—

(a) *Fatty and Rosin Acids.*—10 gms. hard soap used.

Bottle + filter paper + fatty acids	= 39·276 gms.
Bottle + filter paper	= 32·174 "
Fatty acids	= 7·102 "
	= 71·02 per cent.

(b) *Total Alkali.*—Filtrate from above fatty acid determination.

c.cs. of normal H_2SO_4 added	= 50·0 c.cs.
c.cs. of normal NaOH required to titrate back	= 24·2 "
Normal acid used by the total alkali . . .	= 25·8 "

1 c.cs. normal H_2SO_4 = 0·031 gm. Na_2O
25·8 " " " = 0·7998 gm. Na_2O
∴ 10 gms. soap contain 0·7998 gm. total alkali
100 " " " 7·99 gms. Na_2O,
Total alkali . . = 7·99 per cent. as Na_2O

Another method for estimating the total fatty acids is as follows:—

10 gms. of the soap is dissolved in hot water and the fatty acids liberated by the addition of a slight excess of dilute sulphuric acid. The liquid is then heated in the water bath until the fatty acids separate. Exactly 10 gms. of pure beeswax is added, and the whole heated until the wax has completely melted. It is then allowed to cool and the hard cake of fatty matter carefully transferred to a clean beaker. To this, 200 c.cs. of distilled water is added, and the whole heated for 20 minutes in the water bath, after which it is allowed to cool. The cake of fatty matter is washed once again as above and then drained on a clean filter paper. When drained it is transferred to a weighed glass dish and dried in the steam oven until constant in weight. Before calculating the percentage of fatty matter, allowance must be made for the quantity of beeswax added.

Example.—10 gms. of soap used.

Dish + fatty acids + beeswax	= 43·853 gms.
Dish alone	= 26·803 ,,
Fatty acids + beeswax . . .	= 17·050 ,,
Weight of beeswax added . .	= 10·000 ,,
∴ weight of fatty acids . .	= 7·050 ,,

Fatty acids = 70·5 per cent.

Rosin Acids.—Rosin acids may be tested for qualitatively by the Liebermann-Storch reaction.

A few drops of the fatty acids are warmed with 2–3 c.cs. of acetic anhydride. The mixture is allowed to cool, and one drop of pure sulphuric acid added. A fugitive violet colour will indicate the presence of rosin acids.

The quantitative estimation of rosin acids is usually carried out by the Twitchell esterification method. Quite recently, however, a more simple process has been devised by Fortini,[1] which appears to give satisfactory results.

2 gms. of the fatty acids are dissolved in 50 c.cs. of petroleum ether B.P. 40°–70° C. and the solution transferred to a separate funnel. It is then nitrated by shaking with 10 c.cs. of a specially prepared HNO_3, made by mixing 25 c.cs. of fuming HNO_3 (S.G. 1·52) and 75 c.cs. of HNO_3 (S.G. 1·48). To the mixed acids is added a little urea to destroy any nitrous acid, and render the solution colourless.

After shaking, the solution is cooled if necessary, and allowed to separate. The end of the reaction is indicated by the petrol ether layer turning from a green colour to a pale yellow. The acid layer is separated and the etheral solution again nitrated with 5 c.cs. of the prepared HNO_3. The acid layer is separated off and the ether washed, first with HNO_3 and then distilled water. It is then filtered through a dry filter paper and the filtrate collected in a clean, dried and weighed flask. The filter paper should be washed once or twice with small quantities of petrol ether. The ether is then distilled off and the residue of *fatty acids only* dried at 100° C. and weighed. The weight of fatty acids found, deducted from 2 gms., will give the quantity of rosin acids in 2 gms. of the mixed acids.

Example.—2·52 gms. of the mixed fatty and rosin acids used.

Flask + fatty acids . . .	= 27·536 gms.
Flask	= 25·453 ,,
Fatty acids	= 2·083 ,,

$$\therefore \text{ Rosin acids} = (2{\cdot}52 - 2{\cdot}083) \text{ gms.}$$
$$= 0{\cdot}437 \text{ gm.}$$

$$\text{Per cent. of rosin acids} = \frac{100 \times 0{\cdot}437}{2{\cdot}520}$$
$$= 17{\cdot}3 \text{ per cent.}$$

Assuming the total fatty and rosin acid contents of the soap to be 70·5 per cent., the percentage of the rosin acids in the original soap would be

$$\frac{70{\cdot}5 \times 17{\cdot}3}{100}$$
$$= 12{\cdot}19 \text{ per cent.}$$

Free Caustic Alkali.—5 gms. of the soap is dissolved in 100–150 c.cs. of recently boiled alcohol of 95 per cent. strength. When dissolved, the solution is filtered, and any residue on the paper washed with alcohol. The filtrate is titrated *at once* with $\frac{N}{10}$ HCl, using phenol phthalein as indicator.

$$1 \text{ c.c. } \frac{N}{10} \text{HCl} = 0{\cdot}004 \text{ gm. NaOH};$$
or
$$= 0{\cdot}0056 \text{ gm. KOH}$$

The alcohol used for this determination should be made neutral to phenol phthalein.

If the filtrate does not react alkaline to the indicator, free fatty acids may be present, and in that case the alcoholic solution is titrated with $\frac{N}{10}$ NaOH until the phenol phthalein is permanently reddened.

$$1 \text{ c.c. } \frac{N}{10} \text{NaOH} = 0{\cdot}0282 \text{ gm. oleic acid}$$

Alkaline Carbonate.—The residue on the filter paper in the above determination is washed with hot distilled water, and the filtrate collected in a clean flask. The alkali dissolved is then titrated with $\frac{N}{10}$ HCl using methyl orange as indicator. This gives the alkali as carbonate in 5 gms. of the original soap.

$$1 \text{ c.c. } \frac{N}{10} \text{HCl} = 0{\cdot}0053 \text{ gm. } Na_2CO_3$$
or
$$= 0{\cdot}0069 \text{ gm. } K_2CO_3$$

This last titration will also include any silicate or borate present, as both these substances react alkaline to methyl orange.

Combined Alkali.—This is obtained by subtracting the sum of the free alkali (calculated as Na_2O) and alkaline carbonates (calculated as Na_2O) from the total alkali as Na_2O. In the case of soft soaps the alkali is calculated as K_2O.

Silicates.—The solution remaining after titrating the alkaline carbonate is rendered acid with an excess of HCl, evaporated to dryness and ignited. The residue is dissolved in dilute HCl, boiled and filtered. The insoluble silica is well washed with hot distilled water, dried, ignited in a tared crucible and weighed as SiO_2. This gives the amount of silica present as silicate in 5 gms. of soap.

$$SiO_2 \text{ into } Na_2Si_4O_9 \text{ (water-glass)} = 1{\cdot}256$$

Moisture.—Moisture in soap may be estimated by any one of the following methods:—

(*a*) 2 gms. of the soap is weighed into a glass basin of about 7·5 cms. diameter and dried at 60° C. for 1 hour. 50 c.cs. of absolute alcohol is then added and the solution evaporated to dryness. The residue is dried in the hot air oven at 105° C. for 2 hours, then cooled and weighed. The loss in weight is calculated as moisture.

The above method is that issued by the U.S. Bureau of Standards.[2]

(*b*) A known weight of the sample is heated in a tared crucible on a sand bath or over a small flame until all moisture has been expelled and a watch glass held over the crucible ceases to become moistened.

The crucible is then cooled and weighed. This method gives only approximate results, and duplicate determinations should always be carried out.

(*c*) *Distillation Method.*[3]—15 gms. of the soap is transferred to a distillation flask together with an equal quantity of water-free oleic acid (red oil) and 150 c.cs. of water-saturated xylene (*i.e.* xylene which has been shaken with water and allowed to stand for some time). The mixture is distilled and 85 c.cs. of the distillate collected in a graduated tube which already contains 5 c.cs. of water-saturated xylene. The graduated tube should be in the form of a cylinder holding 120 c.cs., and constricted at the bottom to form a graduated tube of 4 cms. in length and graduated to 0·1 c.c. The distillate is allowed to separate for 30 minutes and the volume of water read off. This represents the moisture in the

quantity of soap taken, from which the percentage can be calculated.

REFERENCES

[1] *Annali Chim. Appl.*, 1918, p. 102; *J.S.C.I.*, 1918, p. 381A.
[2] Circular No. 62, U.S. Bureau of Standards.
[3] *J. Ind. Eng. Chem.*, 1918, p. 598; *J.S.C.I.*, 1918, p. 730A.

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LEATHER CHEMISTRY

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CHAPTER XIII

OILS, FATS, WAXES

OILS and fats are, generally speaking, mixtures of various esters of fatty acids and the tri-hydric alcohol, glycerol $CH_2OH.CHOH.CH_2OH$.

In the case of waxes, the glycerol is replaced by higher mono-hydric alcohols, such as cetyl alcohol $C_{16}H_{33}OH$, and myricyl alcohol $C_{30}H_{61}OH$. Fuller details as to the structure of oils, fats and waxes can be found in the well-known work by Lewkowitsch [1] or the recently published book by Fryer and Weston.[2]

When examining an oil for its purity it is important to bear in mind that it is always necessary to base one's opinion on the results of a complete examination, and not merely on the results of one or two determinations.

It is, of course, impossible to deal very fully with this subject within the limits of a single chapter, so that more detailed information should be sought for in the standard works already referred to.

The following are the determinations usually made on a sample of oil or fat:—

Moisture.—2 gms. of the oil or fat is weighed into a tared crucible and carefully heated over a very small flame until the cracking and frothing, which at first takes place, ceases and the first signs of small puffs of oil vapour are seen. The crucible is then cooled down and weighed. The loss in weight can be taken to represent moisture.

This loss on heating will naturally include any other volatile constituents present, but it is accurate enough for technical purposes. This method is not, however, accurate in cases where drying oils are present. A more accurate method is to heat the oil in a flask on a water bath, and collect the water driven off in a weighed calcium chloride tube, a current of an inert and dry gas being passed through the flask during heating.

As a general rule, it may be taken that water is practically absent if the oil does not "crack" or "spit" on heating over a naked flame.

Melting Point.—Solid fats do not have a very definite melting point owing to the fact that in the majority of cases the fat is a mixture of two or more compounds. The most widely used method is the capillary tube method. A piece of ordinary thin walled glass tubing is drawn out so as to form a capillary tube having a diameter of about 1 mm. This is allowed to cool and then cut by means of a file into the desired length (about 4 cms.). A little of the fat is melted in a basin and a small quantity introduced into the capillary tube. This is then allowed to cool and set for a period of 24 hours, or longer if possible. The tube is attached to the stem of a thermometer by means of two small rubber rings (these can be cut from a piece of rubber tubing) and then suspended in a beaker of water, as shown in Fig. 5. The water is gradually heated with a small flame, during which time it is stirred with the stirrer. The temperature at which the fat melts to a clear liquid is noted. The fat may rise in the tube before it is completely melted, so that this indication should not be taken as the M.P.

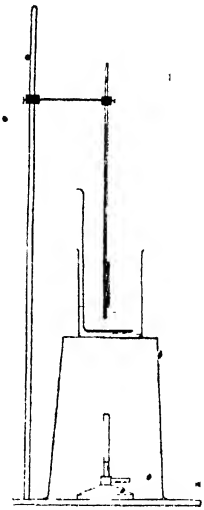

FIG. 5.—Melting Point Apparatus.

It is essential that the fat should be allowed to set for a long period after introduction into the capillary tube prior to taking the M.P., otherwise the correct reading will not be recorded. An example quoted by Fryer and Weston (*loc. cit.*) illustrates this point. Tri-stearine, shortly after solidifying had a M.P. of 55° C., but after being allowed to set for a longer period rose to 71° C.

Duplicate determinations should always be made.

Specific Gravity.—The specific gravity of an oil may be conveniently determined by means of a specific gravity bottle or a Sprengel tube (Fig. 6). In this latter method, the tube, together with the small glass caps, are cleaned, dried and weighed. This is best done by suspending the tube from the hook on the balance by a platinum wire. The caps are then

removed and the tube filled by suction with the oil to be examined. This is adjusted to the marks on the arms of the tube by withdrawing the superfluous oil with a piece of clean filter paper. In the case of liquid oils the tube should be adjusted at a temperature of 15·5° C. by immersing the tube for some time in a beaker of water at this temperature. With solid fats, the tube is adjusted at 100° C. by immersing it in a

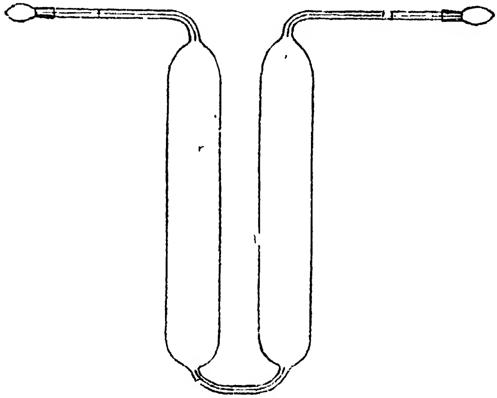

FIG. 6.—Sprengel Tube.

beaker of boiling water, the fat having been previously melted before filling the tube.

After adjusting the oil to the marks, the tube is wiped, the caps replaced, cooled to ordinary room temperature and weighed. The weight of oil or fat introduced is obtained by difference. The tube is then cleaned, and its water capacity ascertained at a temperature of 15·5° C.

The specific gravity of the oil fat will be—

$$\frac{\text{Weight of oil or fat}}{\text{Weight of water}}$$

When both water and oil have been adjusted at 15·5° C. the specific gravity is designated S.G. $\frac{15{\cdot}5^\circ}{15{\cdot}5^\circ}$, while in the case of fats adjusted at 100° C. and the water at 15·5° C., S.G. $\frac{100^\circ\text{ C.}}{15{\cdot}5^\circ\text{ C.}}$

Refractive Index.—The refractive index of an oil is most conveniently determined by means of the Abbé refractometer.

Fig. 7 —Abbe Refractometer.

[To face p. 89.

This type of instrument, now being made in England by Messrs. A. Hilger, is shown in Fig. 7. It has many advantages over other types of refractometers, among which may be mentioned—

(*a*) Only a very small quantity of the oil to be examined is required (a few drops).

(*b*) Measurements can be made with either daylight or artificial light.

(*c*) The refractive index is read off direct from the scale. A uniform temperature is maintained by a current of water, previously heated, circulated through the hollow jacket surrounding each prism.

When the temperature has remained stationary for a time a few drops of the oil are placed between the prisms, and the edge of the shadow observed by looking through the eyepiece brought on to the cross lines in the eyepiece. The refractive index is then read off on the scale.

The following are the average values for the more common oils (reading at 15° C.)

Almond oil . .	1·472–1·473	Neatsfoot oil	1·468–1·470
Castor oil . .	1·479–1·4809	Olive oil . .	1·469–1·471
Cod liver oil .	1·4803–1·482	Rape oil .	1·474–1·476
Brown cod oil .	1·480–1·481	Seal oil . .	1·473–1·479
Cottonseed oil .	1·474–1·4755	Sperm oil .	1·466–1·4673
Lard oil . . .	1·4694	Tung oil .	1·489–1·504
Linseed oil . .	1·482–1·485	Whale oil . .	1·477–1·482
Menhaden oil .	1·481–1·482		

To correct for temperature, the average factor 0·00038 per deg. C. can be used. Thus if an oil had a refractive index 1·463 at 20° C. this would correspond to (5 × 0·00038) + 1·463 at 15° C.

A very complete description of the use of the refractometer is given in a booklet issued by the makers.

Ash.—In the majority of cases the amount of mineral matter in an oil is very small indeed, but at the present time, the determination and examination of the ash of a fat is of value in detecting hardened or hydrogenised oils in mixtures. A known weight of the fat is ignited in a tared crucible and the residual ash cooled and weighed. For the detection of nickle (used as a catalytic agent in the hardening of oils), the ash is dissolved in HCl and the solution evaporated to dryness. The residue is dissolved in a little alcohol and 1–2 drops of ammonia added. This liquid is then treated with

a hot solution of a benzildioxime, when, in the presence of nickel, a red colour or precipitate will be formed.

Acid Value.—The acid value of an oil or fat is expressed as the number of milligrams of KOH required to neutralise the free fatty acids in 1 gm. of the sample. This value is not a "constant" for any specific oil, as the production of free acid is influenced by such factors as age, mode of preparation, etc. 1·5 gms. of the oil is weighed into a conical flask and slightly warmed with 25-30 c.cs. of neutral, 90 per cent. alcohol. A few drops of phenol phthalein solution is added, and the free acidity titrated with $\frac{N}{10}$ NaOH or KOH.

The acid value, according to the above definition, is calculated as follows:—

$$\frac{\text{c.cs. of } \frac{N}{10} \text{ alkali used} \times 5\cdot61}{\text{weight of oil taken}} = \text{acid value}$$

In order to give a clearer solution for titration, some authors recommend as a solvent for the oil a mixture of alcohol and ether, instead of alcohol alone.

As already stated, the acid value of oils vary considerably. Moisture seems to favour the production of free acids and rancidity, while it is known that lipolytic enzymes from oil-bearing seeds pass through into the oil during expression, where they exert their hydrolytic action. Gardner[3] has studied the effects of long storage on the composition of vegetable and animal oils, and, among other things, finds that the acidity increases. This, however, is not so marked in cases where the oil has previously been sterilised.

Saponification Value.—The saponification value of an oil is the number of milligrams of KOH required to saponify one gram of the dry oil or fat. Mineral oils and, to a large extent, rosin oils are not saponifiable, so that the saponification value serves as a means of detecting the latter oils when used as adulterants, etc. The reaction which takes place when an oil is saponified with caustic potash is represented by the following equation:

$$C_3H_5\begin{cases}CO.OR\\CO.OR\\CO.OR\end{cases} + \begin{matrix}KOH\\KOH\\KOH\end{matrix} = C_3H_5\begin{cases}OH\\OH\\OH\end{cases} + \begin{matrix}R.CO.OK\\R.CO.OK\\R.CO.OK\end{matrix}$$

(R = alkyl group)

The method employed for determining the saponification value of a fat is as follows: 1·5 to 2 gms. of the oil or fat is

weighed into a conical flask, and exactly 25 c.cs. of an alcoholic potash solution added. This is prepared by dissolving 40 gms. of pure KOH in the smallest possible quantity of water, and making the solution up to 1000 c.cs. with pure alcohol in a graduated flask. The solution should be allowed to stand for some time, and filtered before use.

Into another flask is pipetted exactly the same volume of KOH as used for the actual determination. In order to

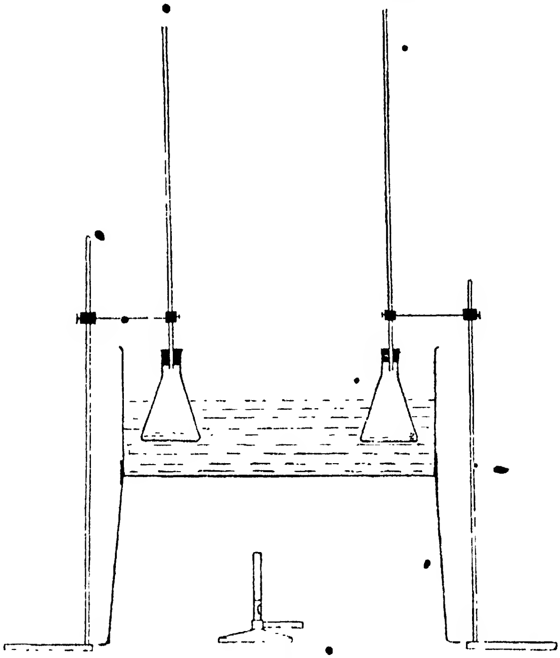

FIG. 8.—Saponification Valve.

obtain correct results it is necessary to take great care in measuring exactly the same volume of KOH in both flasks. To do this, the pipette is allowed to empty, and then, say, three drops over. By allowing the same number of drops to be collected in both cases the volumes in the two flasks will be the same. If preferred, a burette may be used for measuring the volume of alcoholic KOH. Both flasks are then fitted with long glass tubes, to act as air condensers, and heated in a boiling water bath for half an hour (Fig. 8).

During heating the contents of the flasks are occasionally shaken, care being taken that none of the liquid is allowed to get on to the corks. The flasks are then cooled down, and the liquids titrated with $\frac{N}{2}$ HCl, using phenol phthalein as indicator.

The reading obtained in the case of the "blank experiment" will give the amount of alkali added, while the reading from the actual experiment will be equivalent to the KOH remaining unused. The difference between the two will give, therefore, the KOH used for saponifying the oil taken for the determination.

The saponification value can then be calculated thus—

$$\text{saponification value} = \frac{\text{No. of c.cs. } \frac{N}{2} \text{ KOH consumed} \times 56{\cdot}1}{\text{weight of oil taken} \times 2}$$

Example.—1·83 gms. of oil taken, and 25 c.cs. of alcoholic KOH used.

$\frac{N}{2}$ HCl required for the "blank" experiment	=	17·2 c.cs.
$\frac{N}{2}$ HCl " " actual " .	=	4·8 "
$\frac{N}{2}$ KOH used in saponifying the fat	=	12·4 "

$$\text{Saponification value} = \frac{12{\cdot}4 \times 56{\cdot}1}{1{\cdot}83 \times 2} = 190{\cdot}0$$

A low saponification value will indicate the presence of unsaponifiable matter, such as mineral oil, rosin oil, etc., although cases are on record where undoubtedly genuine oils (chiefly fish-liver oils) have contained a large quantity of natural unsaponifiable matter, with a consequent low saponification value. These instances must be borne in mind when expressing an opinion on the purity of fish oils. Chapman[4] examined a sample of fish-liver oil from *Centrophorus granulosis* and *Scymnus lichia*, having a saponification value of only 22·5, and containing 89·1 per cent. of a new hydrocarbon spinacene,[5] $C_{30}H_{50}$.

Iodine Value.—The iodine value of an oil or fat is the percentage of iodine absorbed under standard conditions.

This absorption of iodine is due to the presence in the oil of unsaturated fatty acids and their glycerides.

Based on the iodine value, oils may be divided into three classes, thus—

1. Non-drying oils.	Iodine value, up to 100.
2. Semi-drying oils.	Iodine value, from 100 to 130.
3. Drying oils.	Iodine value, from 130 to 200.

The drying oils are used largely in the manufacture of paints; but their value in this respect is also governed by the nature of the film produced when the oil is exposed to the air. During the drying of oils oxygen is absorbed, which, in the case of paints, is frequently aided by the use of dryers. It must be remembered that all oils having a high iodine are not equally good in drying properties.

Several methods have been proposed for the determination of the iodine value, that described here being Wijs' method.

Great care must be observed as regards the purity of the reagents used in the estimation, and also in the manipulative details.

The solutions required are—

(1) *Iodine Solution.*—10 gms. of pure iodine trichloride is dissolved in 500 c.cs. of glacial acetic acid, and the solution added to one of 11·1 gms. of iodine dissolved in about 500 c.cs. of glacial acetic acid, care being taken to avoid any access of moisture to the solutions. The liquid is then made up to 1500 c.cs. with the same solvent, and transferred to a stoppered, coloured glass bottle.

(2) *Sodium Thiosulphate Solution, $\frac{N}{10}$ Strength.*—Made by dissolving 24·8 gms. of pure $Na_2S_2O_3 . 5H_2O$ in water and making the solution up to 1000 c.cs. with distilled water. This solution is carefully standardised by any of the known methods.

$$1 \text{ c.c. } \frac{N}{10} Na_2S_2O_3 = 0·01269 \text{ gm. I.}$$

(3) *Pure Dry Carbon Tetrachloride* CCl_4.—The tetrachloride is redistilled and dried by standing in contact with a little fused $CaCl_2$. Pure CCl_4 has a B.P. of 76° C.

(4) *Potassium Iodide.*—A 10 per cent. solution of KI, free from iodate, is used.

(5) *Starch Paste.*—0·5 gm. of starch is dissolved by heating in about 20 c.cs. of water, and the solution diluted to 50 c.cs. This must be quite cold when used.

Method.—0·1 to 0·5 gm. of the dry sample, according to

its supposed iodine value, is weighed into a clean, dry, wide-mouthed, stoppered bottle. This is most conveniently done by weighing a small beaker containing a little of the sample, transferring a few drops to the bottle and re-weighing the beaker. The quantity introduced is then ascertained by difference.

10 c.cs. of CCl_4 is added to dissolve the fat, and then 25 c.cs. of the iodine solution pipetted in. The bottle is then tightly stoppered, and the whole allowed to stand for 1 hour. At the end of this time 10 c.cs. of the 10 per cent. KI solution is added, and the residual iodine titrated with $\frac{N}{10} Na_2S_2O_3$, using starch paste towards the end of the titration as indicator.

At the same time as the actual iodine value is being carried out, a blank experiment is made in which the same details are observed as in the actual experiment, with the exception that no oil is used. This solution is titrated in the usual way, and will give a measure of the total iodine added.

The difference between the volume of $\frac{N}{10} Na_2S_2O_3$ required by the blank experiment and that required by the determination proper will give a measure of the iodine absorbed by the oil. An example of the calculations involved is given below.

Example.—

Beaker + oil (first weighing)	=	16·937 gms.
Beaker + oil (second weighing)	=	16·724 „
Oil introduced into bottle	=	0·213 „
Volume of $\frac{N}{10} Na_2S_2O_3$ required by the blank experiment	=	38·2 c.cs.
Volume required by the oil determination .	=	24·0 „
$\frac{N}{10} Na_2S_2O_3$ corresponding to the iodine absorbed	=	14·2 „

Now 1 c.c. $\frac{N}{10} Na_2S_2O_3$ = 0·01269 gm. of iodine,

∴ 14·2 c.cs. „ „ = 0·178198 „ „

0·213 gm. of oil absorb 0·178198 gm. iodine.

∴ 100 gms. will absorb $\frac{0·178198 \times 100}{0·213}$ gms. of iodine

Iodine value = 83·6 per cent.

The Hanûs method for estimating the iodine value is similar in detail to the Wijs method, but the composition of the iodine solution used is different. To prepare this, 13 gms. of iodine is dissolved in about 500 c.cs. of glacial acetic acid, and 8 gms. of bromine added. The solution is then made up to 1000 c.cs. with glacial acetic acid.

Hehner Value.—The Hehner value is the percentage of insoluble fatty acids, together with unsaponifiable matter present in the oil or fat.

5–10 gms. of the oil is saponified by boiling with an excess of alcoholic potash, about 50 c.cs. of the solution described on p. 91. The soap solution thus formed is transferred to an evaporating basin, and taken to dryness on the water bath, to expel the alcohol. The residue of soap is dissolved in about 200 c.cs. of hot water, and the fatty acids liberated from the solution by the addition of a slight excess of dilute sulphuric acid. The liquid is then heated on the water bath until the fatty acids separate out as a clear, oily layer. The fatty acids are then filtered through a weighed filter paper as described in the estimation of the fatty acids in soap (see p. 78).

Example of Calculation.—7·325 gms. of the fat taken and saponified, etc., as above.

Beaker + filter paper + fatty acids .	=	34·217 gms.
Beaker + filter paper	=	27·257
Fatty acids	=	6·960

$$\text{Hehner value} = \frac{6{\cdot}960 \times 100}{7{\cdot}325} = 95{\cdot}0 \text{ per cent.}$$

Oxidised Fatty Acids.—Oxidised fatty acids have the property of being insoluble in petroleum ether, but soluble in alcohol. Such oxidised acids are found to a varied extent in degras.

5 gms. of the sample is saponified in the usual way and the soap solution evaporated to dryness in a porcelain dish. The soap is dissolved in hot distilled water and transferred to a separating funnel. The fatty acids are then liberated with an excess of dilute HCl, and the contents of the funnel cooled. The liquid is extracted with petroleum ether to dissolve out the unoxidised acids. The oxidised acids will be found adhering to the side of the separating funnel. The etheral solution is allowed to separate, and the aqueous liquid run off. The etheral solution is filtered, and

the whole of the oxidised acids transferred to the filter paper and washed well with petroleum ether. They are then dissolved in hot alcohol and the solution collected in a weighed flask. The alcohol is evaporated off on the water bath and the residue of oxidised acids dried in the steam oven and weighed.

Example.—5·736 gms. of the oil taken and treated as described.

Flask + oxidised acids . .	=	28·579 gms.
Flask	=	28·326 „
Oxidised acids	=	0·253 „
Percentage of oxidised acids	=	$\frac{100 \times 0{\cdot}253}{5{\cdot}736}$
	=	4·4 per cent.

Examination of the Fatty Acids.—(a) *Titer Test.*—This test resolves itself into the determination of the solidifying point of the fatty acids. The details are as follows:—

The prepared fatty acids are allowed to stand in a cool place overnight and then carefully melted and poured into a large test tube 16 cms. long and 3·5 cms. diameter. The tube should be about half filled. It is then fitted into a bottle 10 cms. wide and 13 cms. high by means of a cork. A delicate thermometer is inserted in the fatty acids, which are stirred until a cloudiness appears throughout the liquid. During solidification the temperature will rise a little. The maximum is noted and recorded as the titer of the fatty acids. During stirring the side of the test tube should not be touched.

(b) *Bromine Derivatives of Fatty Acids.*—When bromine is added to a solution of fatty acids, insoluble bromo-compounds are formed. The octobromides are insoluble in benzene, the octo and hexabromides insoluble in ether, and the three types of bromides, octo, hexa and tetra, are all insoluble in petrol ether. From this it will be seen that the nature of the precipitate will depend upon the solvent used in the experiment.

Total Insoluble Bromides.—1–2 gms. of the fatty acid is dissolved in about 80 c.cs. of petroleum ether, and bromine added very carefully until the solution is coloured red. The flask and its contents are then allowed to stand overnight. The precipitate, consisting of a mixture of octo, hexa and tetrabromides, is filtered off through a weighed filter paper, washed well with petrol ether, dried by exposure to the air and then in the steam oven, and finally weighed.

Octobromides and Hexabromides.—A known weight of the fatty acids is brominated as usual, using ether as the solvent in place of petrol ether. The precipitate will consist of octo and hexabromides only.

Tetrabromides only.—Obtained by difference from the above to determinations.

Octobromides.—1–2 gms. of the fatty acids are brominated with an excess of bromine, using benzene as the solvent for the fatty acids. The precipitate will consist of the octobromides only. The bromides can be used as a valuable means of discriminating between fish and other oils. The bromides of the former, together with those obtained from the fatty acids of marine animal oils, blacken when the M.P. is determined in the usual way. Bromides from other oils do not. Thus, if the bromides turn black, it is an indication of fish oils.

Unsaponifiable Matter.—The unsaponifiable matter will consist of the small quantity of natural unsaponifiables in oils and fats, *i.e.* cholesterol, phytosterol, etc., also mineral oils and waxes and the unsaponifiable portion of any resin oil present. In the case of waxes, the unsaponifiable matter will also contain the higher alcohols present in waxes.

10 gms. of the sample is saponified with alcoholic potash in the usual way, and the soap solution transferred to a basin and evaporated to dryness. The residue is dissolved in hot water, the solution cooled and extracted with four successive 30 c.c. portions of petroleum ether. If, during the extractions a persistent emulsion should be formed, it may be broken up by the addition of a few drops of alcohol to the petroleum ether layer. The etheral extracts are united and washed two or three times with cold, distilled water in a clean separating funnel. This is necessary in order to free the etheral solution from small quantities of soap. The washed solution is transferred to a tared flask and the solvent distilled off and recovered. The residue of unsaponifiable matter is then dried in the steam oven and weighed. This can then be examined to ascertain its nature. With very few exceptions, the unsaponifiable matter in oils is very small. In the case of fish-liver oils, however, it is variable, and it may reach as high as 15 per cent. As a general rule an oil should be looked upon with suspicion if more than 2 per cent. of unsaponifiable matter is found.

Examination of Unsaponifiable Matter.—As stated above, the unsaponifiable matter may contain a phytosterol (from vegetable oils), cholesterol (from animal oils), and in addition,

such substances as paraffin wax, mineral oil, resin oil, etc., which are sometimes used to adulterate the more expensive oils.

The unsaponifiable matter prepared from a considerable quantity of the oil or fat is dissolved in ether and the solution allowed to crystallise. When the ether has evaporated a small quantity of alcohol is added and the solution warmed slightly. It is then allowed to crystallise out slowly. The crystals obtained can then be examined under the microscope and compared with type slides of both cholesterol and phytosterol.

Further information may be gained by taking the melting point of the acetate prepared from the crystals. The crystals obtained above are warmed with a little acetic anhydride. The excess of the anhydride is driven off by evaporating the solution on the water bath. A few cubic centimetres of alcohol is then added and the acetates allowed to crystallise out. The crystals are drained and re-dissolved in alcohol and re-crystallised. As soon as the first crystals have formed, they are collected and the M.P. taken. Further crops of crystals are obtained and the M.P. of each crop taken.

Cholesterol acetate, M.P. 113·0-113·6° C.

The M.P. of phytosterol acetate varies a little according to its origin, but the average is about 125° C., or a little above.

In cases where a mixture of cholesterol acetate and phytosterol acetate is obtained, the M.P. of the different crops of crystals will vary.

For further details as to the examination of the unsaponifiable matter, standard works of reference should be consulted.

Rosin oil in the unsaponifiable matter would be best detected by examining the fatty acids for rosin acids which generally accompany rosin oils. This may be done by the Liebermann-Storch reaction (see p. 80).

Specific Temperature Reaction.—This is a modification by Thompson and Ballantyne of the original Maumené test. This is determined as follows :—50 gms. of the oil is weighed into a beaker of about 250 c.c. capacity. This beaker is then put into a nest of cotton wool in a larger beaker or cardboard box. The temperature of the oil is carefully taken and recorded. 10 c.cs. of pure sulphuric acid is now run in from a pipette and the mixture of oil and acid constantly stirred. The maximum temperature attained is noted, and the increase in temperature obtained by subtraction. The experiment is now repeated in the same beaker (after being well cleaned), using, in the place of oil, 50 c.cs. of distilled water. It is

imperative that the initial temperature of the oil, water and acid used should be the same. The increase in temperature of the water and acid mixture is ascertained. The specific temperature reaction is then calculated.

$$\frac{\text{Increase in temperature of the oil} \times 100}{\text{Increase in temperature of the water}}$$

Acetyl Value.—The acetyl value is based on the fact that when a hydroxylated compound is boiled with acetic anhydride, the hydrogen atom of the OH group is replaced by an acetyl group ($CH_3 . CO$).

This reaction takes with hydroxylated fatty acids and their glycerides and the alcoholic compounds present in waxes. As determined, the acetyl value is the number of milligrams of KOH required to neutralise the acetic acid produced from 1 gm. of the acetylated oil, etc.

According to Lewkowitsch the most convenient method is as follows:—A suitable quantity of the oil is acetylated by boiling with about twice its weight of acetic anhydride in a round bottomed flask under a reflux condenser. The acetylated product is transferred to a large beaker and boiled with 600 c.cs. of water for half an hour, a piece of broken tile being added to prevent bumping. The liquid is allowed to separate and the aqueous solution syphoned off. The acetylated oil is again washed by boiling with distilled water until the washings cease to redden a piece of blue litmus paper.

Prolonged washing should be avoided, otherwise slight dissociation of the acetyl product will take place and a low acetyl value result. The washed compound is then filtered to remove water, the filtering apparatus being placed in a water oven. A known weight of the acetylated oil prepared as above is saponified by boiling with an excess of alcoholic potash. The soap solution is transferred to an evaporating basin and the alcohol expelled by boiling

The soap solution is transferred to a round bottomed flask and an excess of 10 per cent. sulphuric acid added. This is to liberate the acetic acid from the potassium acetate formed on saponifying the acetylated oil. The flask is connected up to a steam distillation apparatus at once, and the acetic acid distilled over into a clean flask. In order to make sure that all has been distilled it is advisable to collect the distillate in two portions, *i.e.* the first 500 c.cs. and the next 150 c.cs. Both are then titrated with $\frac{N}{10}$ NaOH, using phenol phthalein as indicator. If the distillation has been carried out completely

the second 150 c.cs of distillate will not require more than 0·1 to 0·2 c.c. of alkali for neutralising.

The acetyl value is then—

$$\frac{\text{No. of c.cs. alkali required} \times 5{\cdot}61}{\text{Weight of acetylated oil taken}}$$

The acetyl value is of importance in determining the purity of castor oil. Any adulteration of the oil generally leads to the lowering of the acetyl value.

Some general note and information on oils used in the leather industry are given below.

Cod Oil.—The quality of cod oil varies considerably, depending chiefly upon the method of preparation from the fish livers. Samples often contain considerable quantities of foots or stearine. This, in the better quality oil, is removed by racking, which consists in allowing the solid material to settle out in large tanks. The iodine value of samples which have been racked is usually about 172, while the unracked oil gives a lower figure. The unsaponifiable matter is about 1 per cent. The addition of shark-liver oil increases the percentage of unsaponifiables. Hoppenstedt gives the following method for detecting Menhaden oil in cod-liver oil:—5 c.cs. of the oil is well shaken with 5 c.cs. of acetone and then 1 c.c. of conc. HCl. The whole is vigorously shaken for 1 minute. 5 c.cs. of petrol ether is added, shaken, and allowed to separate. With Menhaden oil the lower layer will be of an intense blue-green colour, whereas with pure cod oil only a yellowish tinge will be given. The test is not sensitive with less than 20 per cent. Menhaden oil.

Mineral oil will increase the unsaponifiable matter, and resin oil, if suspected, can be tested for by the Liebermann-Storch reaction (p. 80).

A very interesting account of the preparation of fish oils in general has been published by the Imperial Institute.[7]

Linseed Oil.—If exposed to the air, especially in thin layers, linseed oil rapidly absorbs oxygen therefrom. Lewkowitsch[8] has shown that if the oil is kept protected from air, light and moisture it will keep unaltered in composition almost indefinitely. Levi and Wilmer[9] give the following figures of aged linseed oil which have been known to stand the test of a practical trial in the manufacture of enamel leathers and have adopted them as a standard upon which to judge other linseed oils intended for the same purpose:—

	Aged Calcutta.	Aged American.
Specific gravity at 20° C.	0·932	0·946
Hehner value	96·57	92·0
Saponification value	182·2	186·3
Iodine value	185·7	183·3
Fatty acids—		
Titer test	16·0° C.	12·0° C
Saponification value	196·5	185·5
Iodine value	189·6	187·0

The presence of cottonseed oil in linseed oil can be ascertained by the Halphen test. 2 c.cs. of the suspected oil is dissolved in 2 c.cs. of amyl alcohol and 2 c.cs. of a 1 per cent. solution of sulphur in carbon di-sulphide added. The mixture is heated in the water bath for a short time. If cottonseed oil is present a deep red coloration will be produced after about 10 minutes' heating. To make sure, the liquid should be heated for 30 minutes before deciding on the sample.

Another delicate test for the presence of cottonseed oil in mixture is the Becchi silver nitrate test.

The fatty acids from the suspected oil are prepared in the usual way, and about 5 c.cs. dissolved in 12–15 c.cs. of 90 per cent. alcohol. 2 c.cs. of a 3 per cent. solution of silver nitrate is added, and the whole heated in a water bath until the volume has been reduced to about 8–10 c.cs. If cottonseed oil is present, the liquid will darken in colour and the fatty acids will turn a black or dark brown colour. This test does not respond with cottonseed oil which has been heated 200°–250° C.

Neat's-foot Oil.—Neat's-foot oil is prepared from the hoofs of cattle which are steamed and the oil skimmed from the surface of the liquor. This oil is particularly favoured for the making of fat liquors.

Samples examined by Fahrion[10] gave the following figures :—

Acid value.	Saponification value.	Iodine value.	M.P. Fatty acids.
9·0	197·6	85·2	28° C.
2·7	195·8	68·5	29° C.
4·7	197·3	59·7	37° C.
2·4	193·4	71·5	29° C.
6·8	196·1	64·3	34° C.
6·6	190·3	76·5	30° C.
4·0	189·0	76·7	26° C.

Adulteration with cottonseed oil can be tested for by the tests already given under this oil.

Castor oil.—Castor oil is distinguished by its high specific gravity and its solubility in alcohol. The acetyl value is high, being on the average 150. It is used as a constituent of fat liquors and in the manufacture of turkey red oil (sulphonated castor oil).

Tallow.—Fresh beef tallow can be readily distinguished from mutton tallow by the odour, that of the latter being rather unpleasant. The melting point of tallow varies and is between 42 48° C. The acid value of good tallow for the leather trade should not be above 20·0. Adulteration with paraffin wax can be detected by the unsaponifiable matter, which in such a case would be considerably increased. If low-grade distilled grease has been added the acid value will be high.

Beeswax.—Beeswax of commerce is the wax deposited by the common bee. Its melting point is 63°-65° C.

The addition of stearic acid would be indicated by a high acid value. The following test due to Weinwurm [11] will prove any adulteration with either paraffin wax or ceresin (refined ozokerite, a mineral wax).

A small quantity of the sample is saponified with alcoholic KOH, and the alcohol evaporated off on the water bath. 20 c.cs. of glycerol is added to the residue and the liquid heated on the water bath; 100 c.cs. of boiling water is added, which, in the case of genuine beeswax, will result in a clear solution. In the presence of paraffin wax or ceresin, the solution will either turn very cloudy or deposit a precipitate.

Sulphonated Oils.—Until within recent years sulphonated oils were prepared by sulphonating vegetable, animal and fish oils, but at the present time almost any oil can be rendered soluble by treatment with sulphuric acid. The details of such processes are kept very secret, and very little is known about them.

As regards the sulphonation of the fixed oils, some valuable work has been done by Radcliffe and Medofski.[12] These authors give a summary of previous work done and an account of their own research into the subject.

In the chemical examination of sulphonated oils, the following determinations should be carried out:—

Moisture.—This is estimated by heating a known weight of the oil in a tared crucible, as already described (see p. 86).

This is not quite accurate as it will include any free ammonia present, but will be found near enough for technical

work. The amount of water in sulphonated oils varies considerably, and may reach as high as 25–30 per cent.

Ash.—The total ash is determined in the usual way, using for preference, the residue from the determination of the water. If more than 1 per cent. is found, it may point to the use of soda in its manufacture. On the other hand, it may be due to insufficient settling out of the oil during washing, for this latter purpose NaCl or Na_2SO_4 being chiefly used.

The ash should be examined for chlorides. If present in any quantity, it may be taken as a sure indication of the use of salt for washing.

Ammonia.—A few cubic centimetres of the oil is diluted with a little distilled water and made alkaline with NaOH. On heating, any ammonia present will be detected by the odour produced. This will indicate that ammonia was used for neutralising the oil after sulphonation and washing. In some cases a mixture of NaOH and ammonia is used for this purpose.

The total ammonia can be estimated by diluting a known weight of the oil with water, making alkaline with NaOH and distilling the ammonia into a solution of boric acid. The ammonia collected is then titrated with standard acid.

Total Fatty Matter.—An approximate idea of the total fatty matter may be obtained by difference, *i.e.* the sum of the moisture and ash deducted from 100.

A more accurate method is as follows:—

5 gms. of the oil is weighed into a basin and 20 c.cs. of water added. If the solution is turbid, a few drops of ammonia are added to make it clear. (If the solution is turbid, it may be taken that either mineral oil, resin oil, or unsulphonated oil is present.)

15 c.cs. of 50 per cent. H_2SO_4 is then added and the whole heated on the water bath until the fatty matter separates out as a clear oily layer. 10 gms. of pure stearic acid is now added and allowed to melt in completely with the other fatty matter. The liquid is allowed to cool and the cake of fatty matter removed and washed two or three times by boiling with distilled water and cooling as already described. The total fatty matter is dried and weighed. An allowance is made for the stearic acid added before calculating the total fatty matter.

The unsaponifiable matter can be determined as for an ordinary fat. This will give an idea as to the presence of mineral oil. The fatty acids, prepared after saponification of

the oil, should be examined for rosin oil by the Liebermann-Storch test (see p. 80).

Degras.—Degras consists in the main of oxidised fish oil, and was formerly obtained as a by-product in the manufacture of chamois leather. It is now manufactured to a large extent by the oxidation of various fish oils.

Degras invariably contains water, which, in some cases, may amount to 25 per cent.

In addition to the ordinary examination, degras should always be tested for mineral acidity. This can be carried out as follows:

10 gms. of the sample is transferred to a separating funnel containing 50 c.cs. of petrol ether and 100 c.cs. of distilled water. The mixture is gently shaken, to avoid a persistent emulsion, and then allowed to separate out. The aqueous layer is drawn off and a few drops of methyl orange added. In the presence of mineral acids, the methyl orange will turn red. The amount of acid can be determined by titrating the liquid with decinormal caustic soda, and calculated as sulphuric acid.

TABLE V

ANALYTICAL AND PHYSICAL CONSTANTS FOR SOME OILS

	S.G.	Sap value	Iodine value %	Acid value	Hehner value %	Unsap. matter %
Almond oil	·915-·920	188-198	94-102	·7 5 6	96·2	·5
Castor oil	·960 ·968	175 180	82- 89	·3 4·0	--	·3
Cod oil	·926-·928	180-197	155 181	·2- 3·0	95·3	1·0
Cottonseed oil . .	·922-·926	193-195	108-110	·5- 2·0	95-96	·5-1·8
Cottonseed oil (blown)	·972-·976	213 214	56-108	6·0 7·0		1·0
Egg oil	·914-·915	184-190	68- 81	-	—	·2
Herring oil . . .	·920-·940	185-190	145	—	95·6	·9-10
Linseed oil . . .	·931-·936	187-195	170 200	·8- 3·0	95·5	·4-1·2
Lard oil	·914-·917	195-196	52- 80	1·0- 2·0	—	·3-·6
Menhaden	·928-·931	190-193	155-160	7·0-10·0	—	1-2
Neat's-foot oil . .	·915-·917	194-199	66 76	2·0- 4·0	—	·1-·6
Olive oil	·915-·918	185-197	81 87	·4- 7·0	95·0	·4-·9
Palm oil	·921 ·924	196-204	52- 57	20	--	—
Rape oil (colza) . .	·914 ·916	169-175	98 100	1·0- 2·5	95·1	·5-·9
Rape oil (blown) . .	·967-·977	175-250	54- 65	8·0-16·0	—	2-3
Seal oil	·924-·929	188-196	126-145	·4 16·0	95·0	·3-1·4
Sesame oil . . .	·920-·924	188-193	105-110	·2-10	95·7	·9-1·1
Soy bean oil . . .	·925-·927	190-196	124-133	1·0 6·0	95·0	·2-·3
Shark liver oil . .	·915-·918	130-190	110-160	—	—	·3-20
Tung oil	940-·941	191-198	166-174	·0-12 0	96·2	·1
Whale oil	·92 -·925	188-193	120-136	·5- 4 0	93·5	1-3·0
Refined bone oil . .	--	186-192	67- 80	3·0- 9·0	—	—

TABLE VI

ANALYTICAL CONSTANTS FOR SOME FATS AND WAXES

	M.P. deg C.	Sap. value.	Iodine value	Acid value.	Unsap. matter %
Beeswax	62–63	91–96	7–10	16–20	54–55
Beef tallow	40–45	190–196	40–45	—	up to [illegible]
Bone fat	21–23	180–190	40–50	up to 40	1–[illegible]
Cocoanut oil	24–25	250–260	7–10	8–10	0·2–1·0
Candelilla wax	67–70	50–60	—	15–20	—
Carnauba wax	83–84	70–80	10–12	3–4	55–56
Japan wax	50–51	210–220	5–7	6–17	1–2
Lard	40–42	193–197	55–68	1–2	0·3
Mutton tallow	45–52	193–195	35–40	6–7	1–2
Myrtle wax	40–41	—	—		—
Paraffin wax	35–55	—	—		99–100
Sperm oil	(liquid)	120–122	82–87	1–2	40–45
Wool grease	Vary too much to give definite figures.				
Spermaceti	48–50	120–128	up to 5	1·0	—

REFERENCES

1 "Oils, Fats, and Waxes"
2 "Oils, Fats, and Waxes," Camb. Univ. Press, 2 vols.
3 *J. Ind. Eng. Chem.*, 1916, p. 997.
4 *Analyst*, 1917, p. 101.
5 *J.C.S.*, 1917, p. 56.
6 *Coll.*, 1911, p. 169.
7 *Bull. Imp. Inst.*, 1914, p. 251.
8 *J.S.C.I.*, 1890, p. 51.
9 *Jour. Amer. Leather Chem. Assoc.*, 1907, p. 104.
10 *Coll.*, 1911, p. 209.
11 *Chem. Zeit.*, 1897, p. 519.
12 *J. Soc. Dyers Cols.*, 1918, p. 22.

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CHAPTER XIV

THE TANNINS (QUALITATIVE)

THE tannins are astringent substances found in various parts of plants, *e.g.* wood, bark, leaves and roots. Chemically, they belong to the aromatic class of organic compounds, and, on decomposition by appropriate methods, yield simpler substances containing, as a rule, only one benzene nucleus. The exact chemical constitution of the tannins has been the subject of much investigation by Perkin, Fischer, Nierenstein and others, but the consideration of this subject is outside the scope of the present work. A general review of the tannins was published by Nierenstein,[1] while a more recent survey has been written by Perkin and Everest.[2]

From the analytical point of view, the tannins are most conveniently divided into two classes according to the products given on heating, *i.e.* catechol group, and pyrogallol group.

In addition, many other qualitative tests can be applied in order to establish the identity of the tannin in the various tanning materials used in the leather industry.

Heating with Glycerol.—This test, according to Thorpe, is carried out as follows:—

1 gm. of the tannin is heated with 3 c.cs. of glycerol to 200° C. for 20 minutes. The mixture is cooled, diluted with a little distilled water, and the solution extracted with ether. The etheral solution is separated and evaporated to dryness. The residue is dissolved in a small volume of water and tested for catechol or pyrogallol.

	Catechol.	Pyrogallol.
Iron alum solution	Green colour	Bluish black, and finally brown
Bromine water	ppt.	No ppt.
Lime water	No reaction	Violet colour.

Reaction with Iron Salts.—A few cubic centimetres of the weak tannin solution is treated with two or three drops of a 1–2 per cent. solution of iron alum. Catechol tannins give a green, while the pyrogallol tannins give a blue-black coloration. Mineral acids interfere with this reaction, and for this reason ferric chloride, which is usually acid, should not be used as the reagent.

Reaction with Lead Acetate.—This reagent gives a precipitate with all tannins, but the presence of acetic acid prevents the precipitation of the catechol tannins. 5 c.cs. of a weak solution of the tannin is treated with 2 c.cs. of acetic acid, and 4–5 c.cs. of lead acetate. Precipitation will take place only if a pyrogallol tannin is present.

For other details concerning this test a paper by Stiasny and Wilkinson [3] should be consulted.

Reaction with Gelatine and Salt Solution.—The test solution used is made by dissolving 1 gm. of gelatine in 100 c.cs. of 10 per cent. sodium chloride solution. A few drops of this reagent is added to a little of the weak tannin solution to be tested. All tannins give a precipitate, but excess of the gelatine solution is to be avoided. It must be remembered that, although all tannins give a precipitate with gelatine, it does not follow that all substances precipitating gelatine are tannins, although it is quite likely that they have tanning properties. Thus wood-pulp, or sulphite cellulose extract, gives the gelatine test, but does not contain tannin.

Formaldehyde Reaction (Stiasny).[1]—Formaldehyde reacts with the tannins in the presence of HCl to give condensation products, catechol tans being completely precipitated.

According to Stiasny and Wilkinson (*loc. cit.*) 50 c.cs. of the tannin solution containing 3 per cent. of tannin is boiled under a reflux condenser with 5 c.cs. of HCl and 10 c.cs. of 40 per cent. formaldehyde for half an hour. The character of the precipitate is noted and the solution is filtered.

10 c.cs. of the filtrate is treated with 1 c.c. of 1 per cent. iron alum solution and 5 gms. of solid sodium acetate. Any coloration of the solution is noted (see table).

Bromine Water Test.—5–10 c.cs. of the weak tannin solution is made faintly acid by adding 1–2 drops of acetic acid and then a slight excess of bromine water added. A precipitate will at once form in the case of a catechol tannin. No precipitate is formed with pyrogallol tannins.

Eitner-Philip. Ammonium Sulphide Test.—25 c.cs. of the tannin solution containing 2·5 per cent. of tannin is boiled for 2 minutes with 2–3 drops of concentrated sulphuric

acid. The solution is cooled down, 5 gms. of common salt added, and, after standing for a short time, filtered. To 2–3 c.cs. of the filtrate is added 10–15 drops of yellow ammonium sulphide solution, previously diluted with 15 c.cs. of water. All pyrogallol tannins give a precipitate in this test in addition to mimosa and malet, which otherwise behave as catechol tannins. (For reactions, see table, p. 116.)

Ethyl Acetate Figure (Procter).—The ethyl acetate figure as expressed is the percentage of the total soluble matter of a tannin solution or extract, etc., soluble in ethyl acetate.

25 c.cs. of the tannin solution containing about 0·4 per cent. of tannin is evaporated to dryness in a weighed basin and the residue dried at 100–105° C. and weighed. This gives the weight of total soluble matter in 25 c.cs. of the solution. Another 25 c.cs. of the solution is extracted three or four times with 25 c.cs. of ethyl acetate, using fresh solvent for each extraction. The aqueous solution is then freed from ethyl acetate by a current of air, and 20 c.cs. evaporated to dryness and the residue dried and weighed. This gives the non-extracted matter in 20 c.cs. of the solution. The weight obtained is multiplied by $\frac{5}{4}$ to give the quantity in 25 c.cs. of the original solution. The difference between the total soluble matter and the non-extracted matter will give the amount extracted by ethyl acetate. This, calculated as the percentage of the total soluble matter, represents the ethyl acetate figure which is characteristic for many materials.

Example.—

Basin + residue from 25 c.cs. of solution	=	25·879 gms.
Basin	=	25·734 ,,
Weight of residue	=	0·145 ,,
Basin + residue from 20 c.cs. of extracted solution	=	19·668 ,,
Basin	=	19·598 ,,
Weight of extracted residue from 20 c.cs.	=	0·070 ,,
∴ weight of residue from 25 c.cs. . . .	=	0·0875 ,,
Ethyl acetate extracted matter in 25 c.cs.	=	(0·145–0·0875) gm.
	=	0·0575 gm.
Per cent. of total solids soluble in ethyl acetate	=	$\frac{100 \times 0·0575}{0·145}$
	=	39·6 per cent.

A convenient form of apparatus for the determination of the ethyl acetate figure, which is both accurate and compact, is described by Blockey.[5]

Alcohol Figure.—This figure is expressed as the percentage of total soluble matter of the tannin solution which is precipitated by alcohol, and was first suggested by Procter as a means of differentiating between certain tannins.

A solution of the tanning material is prepared so as to contain about 3 per cent. of tannin. 10 c.cs. of this is measured into a 100 c.c. graduated flask and made up to the 100 c.c. mark with 95 per cent. alcohol. After standing for an hour, the well mixed solution is filtered, and 50 c.cs. of the filtrate (= 5 c.cs. of the original solution) evaporated to dryness in a weighed dish. The residue is dried to constant weight in a steam oven and weighed. This gives the weight of alcohol soluble matter in 5 c.cs. of the solution. The total soluble matter in 10 c.cs. of the original solution is also determined in the usual way. To ascertain the alcohol figure the following calculations are necessary:—

Example.—

Basin + total residue from 10 c.cs. soln.	= 19·994 gms.
Basin alone	= 19·732 „
Total residue from 10 c.cs.	= 0·262 „
Basin + 50 c.cs. of alcoholic soln. . . .	= 22·593 „
Basin alone	= 22·489 „
Alcohol soluble from 5 c.cs. orig. soln.	= 0·104 „
„ „ 10 c.cs. „	= 0·208 „
∴ alcohol insoluble in 10 c.cs. of soln. .	= (0·262 − 0·208) gm.
	= 0·054 gm.

The percentage of alcohol insoluble matter expressed on the total soluble matter is therefore—

$$\frac{100 \times 0·054}{0·262} = 20·6 \text{ per cent.}$$

The qualitative distinction between the various tannins has been largely investigated by Stiasny and his co-workers, and a considerable amount of the investigation was published by Stiasny [6] in a condensed form, useful for reference.

The following scheme is taken from this paper:—

The scheme divides the tannins into three main groups, each of which is further subdivided into two divisions.

The first main divisions are based on the character of the formaldehyde test.

Group I.—Complete precipitate: the filtrate gives neither gelatine test nor iron test.

Tests for confirmation: bromine test (precipitate) and acetic acid-lead acetate test (no precipitate).

Group II.—No precipitation during fifteen minutes' boiling.

Test for confirmation: bromine test (no precipitate); ammonium sulphide test (precipitate).

Group III.—Considerable precipitate during boiling, but distinct iron test of the filtrate.

To Group I. belong: quebracho, mangrove, ulmo, gambier, pinebark, hemlock, mimosa, malet.

To Group II. belong: oak-wood, chestnut-wood, valonia, myrobalans.

To Group III. belong: oakbark, pistacia, lentiscus, sumach, divi-divi, algarobilla, teri, babla, galls.

Having found to which group the tannin belongs, the following tests are made in each group:—

Further testing of Group I.: The ammonium-sulphide test allows a subdivision, in so far as no precipitate is obtained with quebracho, mangrove, ulmo, gambier, pinebark, hemlock (Group IA), while a precipitate is shown by mimosa and malet (Group IB).

Group IA is also characterised by the green coloration produced with iron alum.

Group IB gives a bluish violet with iron alum.[7]

The further way of identifying the tannin in IA or IB, demands the carrying out of all the tests summarised in Table VII. This table also contains the gallic acid value of one gm. of the tannin and the proportion of tans to non-tans in the tanning material.

Potassium cyanide has been suggested by Bennett as a suitable reagent for the differentiation of the tannins.

An excess of a 0·1 per cent. solution of KCN is added to a clear solution of the tanning material and the mixture poured into an excess of hard water (or a 0·05 per cent. solution of $CaCl_2$). All pyrogallol tannins and some of the mixed tannins develop a very distinct precipitate. Catechol tannins do not give a precipitate. The mechanism of the test seems to be obscure, but it is evidently connected with the hardness of the water, as with distilled water the test will not respond. The same investigator[8] has applied cobalt, nitrate, iodine, potassium ferricyanide and sodium arsenate to the differentiation of the tannins.

Cobalt Test.—6-7 c.cs. of the tannin solution of 0·1 per cent. strength is mixed with an equal volume of hydrogen

TABLE VII

50 c.cs. tannin solution (0·4 per cent.) boiled with 25 c.cs. H.CHO – HCl mixture for ½ hour thoroughly cooled and filtered.

Group I.		Group II.		Group III.	
Complete precipitate— Filtrate with iron alum and sodium acetate = no violet colour. Confirming tests— Bromine gives ppt. acetic acid and lead acetate = no ppt.		No ppt. after 15 mins. boiling. Confirming tests— Bromine = no ppt.: ammonium sulphide test = precipitate.		Considerable ppt. after 15 mins. boiling. Filtrate with iron alum and sodium acetate gives deep violet colour.	
The ammonium sulphide test is made on 25 c.cs. of the 2·5 per cent. tannin solution.		5 c.cs. of tannin solution tested by the lead acetate and acetic acid test. The filtrate from this test is treated with iron alum.		The Bromine water test is made on 5 c.cs. of the weak (0·4 per cent.) tannin solution.	
Group IA.	Group IB.	Group IIA.	Group IIB.	Group IIIA.	Group IIIB.
No ppt. Confirm with iron alum = green colour. Quebracho. Mangrove. Ulmo. Gambier. Pine bark. Hemlock.	Ppt. formed. Confirm with iron alum = blue-violet. Mimosa. Mallet.	No coloration. Oak wood. Valonia.	Violet coloration. Chestnut. Myrobalans.	Precipitate. Oak bark. Pistacia.	No ppt. Sumach. Divi-divi. Algarobilla. Galls. Babla. Teri

TABLE VIII

	Formaldehyde-test: During 15 mins. boiling.	Formaldehyde-test: Filtrate + iron alum + sodium acetate.	Bromine test	Ammonium-sulphide test	Lead-acetate test. Filtrate + NaOH	Acetic acid + lead acetate test.	Acetic acid + lead acetate test: Filtrate + iron alum.	Ethyl-acetate figure	Alcohol figure	Gallic acid value of 1 gm tannin (see Coll., 1909, p. 101)	Tans. / Non-tans.
Quebracho . .	ppt.	no coloration	ppt.	no ppt.	yellowish	no ppt.	green	70–80	0–5	0·59	8·0–10·0
Sulphited-quebracho	ppt.	no coloration	ppt	no ppt.	yellowish	no ppt. (but $PbSO_4$)	green	0–70	0–5	0·59	depends on the method of sulphiting
Mangrove	ppt	no coloration	ppt.	no ppt.	colourless	no ppt.	green	0–5	0–5	0·68	2·5– 4·0
Ulmo . .	ppt.	no coloration	ppt.	no ppt.	yellowish	no ppt.	green	70–80	0–5	—	8·0–10·0
Gambier . .	ppt.	no coloration	ppt.	no ppt.	—	no ppt.	green	50–65	5–10	0·56	1·2– 1·5
Mimosa . .	ppt.	no coloration	ppt.	ppt.	colourless	no ppt.	deep bluish violet	30–40	0–5	0·53	2·0– 3·0
Oakbark. .	ppt.	violet	ppt.	ppt.	colourless	ppt.	—	12	17	—	1·0– 1·5
Hemlock .	ppt.	no coloration	ppt.	ppt. (after standing overnight)	yellowish	no ppt.	green	18	9	–	1·0– 2·0
Pistacia . .	ppt.	deep bluish violet	ppt.	ppt.	yellow	ppt.	green and violet	3	29	–	—
Chestnut .	no ppt.	deep bluish violet	no ppt.	ppt.	colourless	ppt.	very faint violet	0–16	10–20	0·56–0·66	2·0– 3·5
Oakwood .	no ppt.	deep bluish violet	no ppt.	ppt.	colourless	ppt.	colourless	0–12	20–30	0·5 –0·56	1·0– 2·0
Myrobalans .	ppt.	deep bluish violet	no ppt.	ppt.	colourless	ppt.	violet	30–50	0–15	0·55–0·60	1·5– 2·5
Sumach . .	ppt.	deep bluish violet	no ppt.	ppt.	yellow	ppt.	violet	40–60	5–20	0·65–0·69	1·5– 1·8
Valonia . .	turbid	deep bluish violet	no ppt.	ppt.	colourless	ppt.	colourless	5–15	20–40	0·55–0·63	2·0– 3·0
Divi-divi .	turbid	deep bluish violet	no ppt.	ppt.	colourless	ppt.	violet	30–50	0–10	—	2
Algarobilla .	turbid	deep bluish violet	no ppt.	ppt.	colourless	ppt.	violet	50–60	0–5	—	2
Wood pulp .	no ppt.	no coloration	no ppt.	not characteristic	deep yellow	no ppt.	colourless	0–5	30–70	0·09–0·14	0·75

peroxide, and three or four drops of cobalt solution added. The colour produced is noted.

The special cobalt solution is prepared as follows:

2·5 gms. of cobalt nitrate dissolved in a small volume of distilled water is added to a solution of 25 gms. of ammonium carbonate in 150 c.cs. of distilled water.

Valonia, chestnut and oakwood give a purple colour.

Sumach, myrobalans, algarobilla, gallic and gallo-tannic acids give an orange colour.

Quebracho, mimosa and gambier give a bright red colour.

Iodine Test. A weak solution of the tannin is diluted with about 500 c.cs. of hard water and 2 c.cs. of a 1 per cent. solution of iodine in potassium iodide added.

Valonia, chestnut and oakwood give a dark blue colour.

Myrobalans, sumach, algarobilla, gallic and gallotannic acids and mimosa give purple-red colour.

Gambier and quebracho give no coloration at all.

Ferricyanide Test. A small crystal of this salt is dissolved in a 10 per cent. solution of ammonia. A few drops of the reagent added to a largely diluted solution of the tannin gives a purple colour in the cases of valonia, oak vood and chestnut.

Sodium Arsenate Test. A solution of sodium arsenate added to a very dilute solution of the tannin produces a green colour in the case of a pyrogallol tannin, and a red colour in the presence of a catechol tannin. The solution is allowed to stand for a little time before deciding on the colour.

Schell's Test. This is a test designed to detect mangrove in quebracho extracts, and is carried as follows: 20 c.cs. of the solution of about 0·3 per cent. tannin strength is heated for a short time to expel any air and then quickly cooled. A small quantity of petrol ether is added, enough to form a good layer on the surface of the solution and 1 c.c. of a 20 per cent. solution of cobalt chloride, and 1 c.c. of ammonia added. Quebracho extract gives a greenish colour, while if mangrove is present a brownish colour will be produced. The author of this test has recently shown[9] that slight alkalinity of the quebracho will interfere with the delicacy of the test. The presence of sulphites also influences the result. The test should therefore be used in conjunction with other tests.

Sulphite-Cellulose Extracts. Sulphite cellulose extract is prepared from the purified liquors obtained in the manufacture of paper pulp by the sulphite process. The concentrated liquor has certain tanning properties, and on this

account coupled with its low price, is frequently used as an adulterant of other more expensive extracts. The extract is sometimes known by the name of wood pulp extract.

The most reliable test for this material is the Procter-Hirst reaction, which is a general lignin reaction.

The test is as follows :—5 c.cs. of the tannin solution to be tested of about 0·4 per cent. tannin strength, is well shaken with exactly 0·5 c.c. of pure aniline. 2 c.c. of concentrated HCl is then added. After 10 minutes the presence of sulphite cellulose extract will be indicated by the formation of a precipitate. There are a few exceptions to the test, as, for example, in the case of sulphited extracts or those prepared under pressure.

Diazobenzene Chloride Reaction.—This reaction was first introduced by Nierenstein [10] and is based on the fact that all catechol tannins give a precipitate of the azo-benzene tannin when treated with diazobenzene chloride. The reagent is added drop by drop to the solution of the tannin to be tested. The precipitate appears at once. No precipitate is produced with pyrogallol tannins.

This reaction has been made the basis of a method for the quantitative estimation of catechol tannins in sumach.[11]

Bennett [12] distinguishes between the tannins of valonia, oakwood and chestnutwood by the following distillation method :—The extract or solution is evaporated to dryness and the residue destructively distilled in a suitable retort or other apparatus. The distillation is carried out until no more distillate can be collected. The total distillate is shaken with a little distilled water and filtered to remove tarry matter. An excess of strong bromine water is then added to the filtrate and the mixture well shaken. Valonia gives a dense yellow crystalline precipitate of tetra-bromo-phenol $C_6H_2Br_3OBr$ M.P. after washing with cold alcohol 139–141° C. Chestnut gives no precipitate whatever, and is readily distinguished from valonia by this test.

Oakwood gives only a slight precipitate of compound, which after re-crystalling from alcohol dilute had an M.P. of 86°–89° C.

Other tests will be dealt with as the occasion arises in the next chapter.

REFERENCES

1 *J. Soc. Dyers Cols.*, 1911, No. 2.
2 "The Natural Organic Colouring Matters," 1918, Chap. ......
3 *Coll.*, 1911, p. 318.
4 *Der. Gerber*, 1905, p. 185.

[5] *Coll.*, 1913, p. 634.
[6] *Ibid.*, 1914, p. 76.
[7] *Ibid.* (London Edition), 1915, p. 56.
[8] *Abstr. Coll.* (London Edition), 1915, p. 61.
[9] *Jour. Soc. Leather Trades Chem.*, 1918, p. 284.
[10] *Coll.*, 1906 (*Jour. Amer. Leather Chem. Assoc.*, 1906, p. 317).
[11] *Ibid.*, 1907, pp. 116, 224, also *Jour. Amer. Leather Chem. Assoc.*, 1907 p. 308.
[12] *J.S.C.I.*, 1914, p. 1186.

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CHAPTER XV

TANNINS (QUANTITATIVE)

THE most reliable method for the estimation of tannin in a tanning material is the Official method of the International Association of Leather Trades' Chemists (now re-formed among Allied countries into the Society of Leather Trades' Chemists). By this method the amount of tanning matter capable of being absorbed by hide powder is estimated, and from the point of view of the tanner, gives an idea of the leather-forming properties of the material. The method is the outcome of much experimental work by Yocum, in America, and Procter and Bennett[1] in England.

The following are the official regulations regarding this method, as laid down by the International Association :—

Paragraph 1. The solution for analysis must contain between 3·5 and 4·5 gms. of tanning matter per litre, and solid materials must be extracted so that the greater part of the tannin is removed at a temperature not exceeding 50° C., but if the Teas Extractor be used, the first portion of the extract shall be removed from the influence of heat as soon as possible.

Paragraph 2. The total solubles must be determined by the evaporation of a measured quantity of the solution previously filtered till optically clear both by reflected and transmitted light; that is, a bright object such as an electric light filament must be distinctly visible through at least 5 cms. thickness and a layer of 1 cm. deep in a beaker placed in a good light on black glass or black glazed paper must appear dark and free from opalescence when viewed from above. Any necessary mode of filtration may be employed, but if such filtration causes any appreciable loss when applied to a clear solution, a correction must be determined and applied as described in sect. 6. Filtration shall take place between the temperatures of 15° C. and 20° C. Evaporation to dryness shall take place between 98·5° C. and 100° C. in shallow flat-bottomed basins, which shall afterwards be dried until constant at the same temperature, and cooled before weighing for not less than 20 minutes in air-tight desiccators over dry calcium chloride.

Paragraph 3. The total solids must be determined by drying a weighed portion of the material, or a measured portion of its uniform turbid solution at a temperature between 98·5° C. and 100° C. in shallow flat-bottomed basins which shall afterwards be dried until constant at the same temperature and cooled before weighing for not less than 20 minutes in air-tight desiccators over dry calcium chloride. "Moisture" is the difference between 100 and the percentage of total solids, and "insoluble" the difference between "total solids" and "total solubles."

Paragraph 4. *Non-tannins.* —The solution must be detannised by shaking with chromed hide powder till no turbidity or opalescence can be produced in the clear solution by salted gelatine. The chromed powder must be added in one quantity equal to 6·0 to 6·5 gms. of dry hide per 100 c.cs. of the tanning solution, and must contain not less than 0·2 and not more than 1 per cent. of chromium reckoned on the dry weight, and must be so washed that in a blank experiment with distilled water, not more than 5 mgrs. of solid residue shall be left on evaporation of 100 c.cs. All water contained in the powder should be determined and allowed for as water of dilution.

The following sections give the detailed method of carrying out the analysis adopted by the I.A.L.T.C. for the use of its own members.

Paragraph 5. *Preparation of Infusion.*- Such a quantity of material shall be employed as will give a solution containing as nearly as possible 4 gms. of tanning matter per litre, and not less than 3·5 or more than 4·5 gms. Liquid extracts shall be weighed in a basin or beaker and washed with boiling distilled water into a litre flask, filled up to the mark with boiling water, and well mixed, and rapidly cooled to a temperature 17·5° C., after which it shall be accurately made up to the mark, again well mixed, and filtration at once proceeded with. Sumach and myrobalans extracts should be dissolved at a lower temperature.

Solid extracts shall be dissolved by stirring in a beaker with successive quantities of boiling water, the dissolved portions being poured into a litre flask, and the undissolved being allowed to settle and treated with further portions of boiling water. After the whole of the soluble matter is dissolved the solution is treated similarly to that of a liquid extract.

Solid tanning materials, previously ground till they will pass through a sieve of 5 wires per centimetre, are extracted in Koch's or Procter's extractor with 500 c.cs. of water at a temperature not exceeding 50° C. and the extraction continued with boiling water till the filtrate amounts to 1 litre. It is desirable to allow the material to soak for some hours before commencing the percolation, which should occupy not less than three hours, so as to extract the maximum of tannin. Any remaining solubles in the material must be neglected, or reported separately as "difficultly soluble" substances. The volume of liquid in the flask must after cooling be accurately made up to 1 litre.

Paragraph 6. *Filtration.*—The infusion shall be filtered till optically clear (see sect. 2). No correction for absorption is needed for the Berkefeld candle, or for S. and S. 590 paper if a sufficient quantity (250–300 c.cs.) is rejected before measuring the quantity for evaporation; and the solution may be passed through repeatedly to obtain a clear filtrate. If other methods of filtration are employed the average correction necessary must be determined in the following manner: About 500 c.cs. of the same or a similar tanning solution is filtered perfectly clear, and after thorough mixing 50 c cs. is evaporated to determine "total soluble No. 1." A further portion is now filtered in the exact method for which the correction is required (time of contact and volume rejected being kept as constant as possible) and 50 c.cs. is evaporated to determine "total soluble No. 2." The difference between No. 1 and No. 2 is the correction sought, which must be added to the weight of the total solubles found in analysis. An alternative method of determining correction, which is equally accurate and often more convenient, is to filter a portion of the tanning solution through the Berkefeld candle till optically clear, which can generally be accomplished by rejecting 300 or 400 c.cs. and returning the remaining filtrate repeatedly; and at the same time to evaporate 50 c.cs. of clear filtrate obtained by the method for which correction is required, when the difference between the residues will be the correction sought.

(NOTE.—It is obvious that an average correction must be obtained from at least 5 determinations. It will be found that this is approximately constant for all materials, and amounts in the case of S. and S. 605, 150 c.cs. being rejected, to about 5 mgrs. per 50 c.cs. and where 2 gms. of kaolin are employed in addition to 7½ mgrs. The kaolin must be previously washed with 75 c.cs. of the same liquor, which is allowed to stand 15 minutes and then poured off. Paper 605 has a special absorption for a yellow colouring matter often contained in sulphited extracts.)

Paragraph 7. Hide powder shall be of woolly texture, thoroughly delimed, preferably with hydrochloric acid, shall not require more than 5 c.cs. or less than 2·5 c.cs. of $\frac{N}{10}$ NaOH or KOH to produce a permanent pink with phenol phthalein on 6½ gms. of the dry powder suspended in water. If the acidity does not fall within these limits it must be corrected by soaking the powder before chroming for 20 minutes in 10–12 times its weight of water to which the requisite calculated quantity of standard alkali or acid has been added. The hide powder must not swell in chroming to such an extent as to render difficult the necessary squeezing to 70–75 per cent. of water, and must be sufficiently free from soluble organic matter to render it possible in the ordinary washing to reduce the total solubles in a blank experiment with distilled water below 5 mgrs. per 100 c.cs. The powder when sent out from the makers

shall not contain more than 12 per cent. of moisture, and shall be sent out in air-tight tins.

The detannisation shall be carried out in the following manner:—

The moisture in the air-dried powder is determined and the quantity equal to 6·5 gms. actual dry hide powder is calculated, which will be practically constant if the powder be kept in an air-tight vessel. Any multiple of this quantity is taken according to the number of analyses to be made, and wet back with approximately 10 times its weight of distilled water (very woolly powders require slightly more than 10 times their weight of water. A powder may be considered "woolly" if it cannot be poured like sand from a beaker).

2 gms. per 100 gms. of dry powder of crystallised chromic chloride $CrCl_3 6H_2O$ is now dissolved in water and made basic with 0·6 gm. Na_2CO_3 by the gradual addition of 11·25 c.cs. of normal Na_2CO_3, thus making the salt correspond to the formula $Cr_2Cl_3(OH)_3$. This solution is added to the powder, and the whole churned for 1 hour. In laboratories where analyses are continually being made, it is more convenient to employ a 10 per cent. stock solution, made by dissolving 100 gms. of $CrCl_3 6H_2O_4$ in a little distilled water in a litre flask, and very slowly adding a solution containing 30 gms. of anhydrous sodium carbonate, with constant stirring, finally making up to mark with distilled water and well mixing. Of this solution 20 c.cs. per 100 gms. or 1·3 c cs. per 6·5 gms. of dry powder should be used.

At the end of one hour the powder is squeezed in linen to free it as far as possible from the residual liquor, and washed and squeezed repeatedly with distilled water, until on adding to 50 c.cs. of the filtrate, 1 drop of 10 per cent. K_2CrO_4 and 4 drops $\frac{N}{10}AgNO_3$, a brick-red colour appears. Four or five squeezings are usually sufficient. Such a filtrate cannot contain more than 0·001 gm. of NaCl in 50 c.cs.

The powder is then squeezed to contain 70–75 per cent. water, and the whole weighed. The quantity Q containing 6·5 gms. dry hide is thus found, weighed out, and added immediately to 100 c.cs. of the unfiltered tannin infusion along with (26·5–Q) of distilled water. The whole is corked up and agitated for 15 minutes in a rotating bottle at not less than 60 revolutions per minute. It is then squeezed immediately through linen, 1 gm. of kaolin added to the filtrate, stirred and filtered through a folded filter of sufficient size to hold the entire filtrate, returning till clear, and 60 c.cs. of the filtrate is evaporated and reckoned as 50 c.cs., or the residue of 50 c.cs. is multiplied by $\frac{6}{5}$. The non-tanning filtrate must give no turbidity with a drop of a 1 per cent. gelatine 10 per cent. salt solution. The kaolin may be used by mixing it with the hide powder in the shaking bottle.

Paragraph 8. The analysis of used liquors and spent tans shall

be made by the same methods as are employed for fresh tanning materials, the liquors or infusions being diluted, or concentrated by boiling *in vacuo*, or in a vessel so closed as to restrict access of air, until the tanning matter is if possible between 3·5 and 4·5 gms. per litre, but in no case beyond a concentration of 10 gms. per litre of total solids, and the weight of hide powder used shall not be varied from 6½ gms.

The results shall be reported as shown by the direct estimation, but it is desirable that in addition efforts shall be made, by determination of acids in the original solution and in the non-tannin residues, to ascertain the amount of lactic and other non-volatile acids absorbed by the hide powder, and hence returned as "tanning matters." In the case of tans it must be clearly stated in the report whether the calculation is on the sample with moisture as received, or upon some arbitrarily assumed percentage of water; and in that of liquors whether the percentage given refers to weight or to grams per 100 c.cs.; and in both cases the specific gravity shall be reported.

Paragraph 9. All evaporation shall be rapidly conducted at steam temperature in shallow flat-bottomed basins of not less than 5·5 cms. diameter to apparent dryness; and shall be subsequently dried between 98° and 100° C. in a water or steam oven until of constant weight, and shall be afterwards cooled in small air-tight desiccators over dry calcium chloride for at least twenty minutes, and then weighed rapidly. Not more than two basins shall be placed in one desiccator, and the basins must not be wiped after removal from the desiccator.

All analyses reported must be the average result of duplicate determinations which must agree in the case of liquid extracts within 0·6 per cent., and of solid extracts within 1·5 per cent., or the analysis shall be repeated till such agreement is obtained.

Preparation of the solution of the material to be analysed by the above Official method:—

It will be noticed that there is a certain limit made for the tannin strength of the solution to be examined, so that the amount of substance to be taken for the preparation of this will vary with differtnt types of material. To prepare 1 litre of the sample, Procter[2] recommends the following quantities be taken:—

	gms.
Solid extracts	5–7
Pasty extracts (S.G. over 1·2)	9–12
Liquid extracts (S.G. 1·15–1·2)	12–18
Liquid extracts (S.G. below 1·15) . . .	18–20
Algarobilla	9
Canaigre	18
Divi-divi	9

	gms.
Oak bark	36
Oak wood	50
Sumach	16
Valonia	14
Hemlock bark	32
Mimosa bark	12
Mangrove bark	10
Myrobalans	12
Quebracho wood	22
Spent tanning materials	50

In the case of barks and other natural materials, the sample is ground in a suitable mill, and the quantity indicated in the above table weighed out and transferred to a Procter's extractor. This is illustrated in Fig. 9.

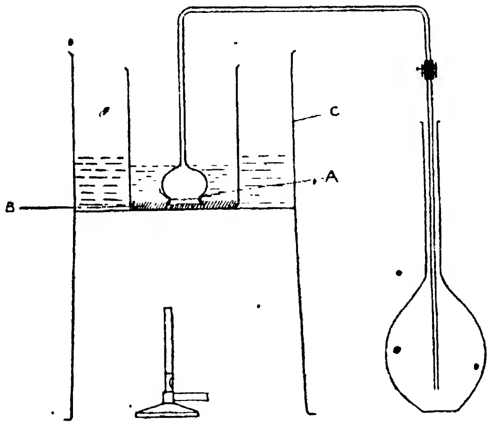

FIG. 9.—Procter's extractor.

A. Inverted thistle funnel over the end of which is a piece of muslin. B. Clean, iron free sand to act as a filter. C. Water bath.

Sufficient distilled water is added to cover the material which is then allowed to soak overnight.

The water bath is heated, and the first 500 c.cs. of liquid extracted below a temperature of 50° C. in accordance with the official regulations, water heated to this temperature being added as extraction proceeds.

After the 500 c.cs. has been collected, the temperature is

gradually increased to 100° C., and the extraction completed up to 1000 c.cs. at this temperature. The solution is then cooled down under the tap and made up to the mark with distilled water.

Canaigre, on account of the large quantity of starch present, should not be boiled as indicated above, but extracted at the lower temperature. Sumach should be extracted as completely as possible at 50°–70° C., as decomposition of the tannin takes place at 100° C. The time required for the extraction is from 3–4 hours.

To prepare a solution of a solid extract, the following procedure is adopted. The necessary quantity of the powdered

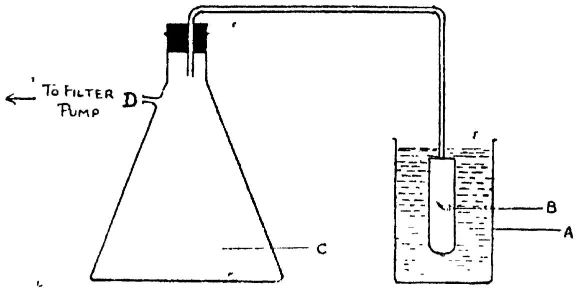

Fig. 10.—Filtration apparatus.

A. Beaker containing the tannin solution to be filtered. B. Berkfeld candle. C. Filtering flask to receive the filtered solution. This flask is connected to pump at D.

sample is weighed into a glass or porcelain basin and the extract washed into a clean beaker with a stream of boiling distilled water. More boiling water is added to the beaker and the liquid stirred with a glass rod until solution is complete. It is then poured into a 1000 c.c. flask, and the beaker washed with boiling distilled water and the washings added to the flask. The contents of the flask are then made up to the mark with boiling distilled water, and cooled rapidly under the tap. The cold solution is then made up to the mark with distilled water and well shaken. With liquid extracts the solution is prepared in the same way, only solution will be more rapid. Sumach extracts should be made up with water at a temperature of 50°–60° C.

Filtering.—The most reliable method of filtering is by using a Berkfeld filtering candle. For this, the apparatus as shown in Fig. 10 will be found most convenient.

The candle, if new, should be soaked in HCl to remove iron and other extractable matter, and then thoroughly washed with distilled water. After use, the film of insoluble matter on the candle can be removed by brushing with an ordinary soft tooth brush.

The first 200 c.cs. of the filtrate is neglected, or used for the estimation of the non-tannins, and 50 c.cs. of the clear filtrate evaporated to dryness in a weighed dish, as described in the official regulations.

Calculation of Results.—As the calculation of results seems at first sight to be somewhat complicated, it will be advisable to give one or two examples.

Example 1.—6 gms. of a Quebracho extract was dissolved in 1 litre, as described above.

Total Solids.—(This includes everything in the extract with the exception of the moisture.) 50 c.cs. evaporated to dryness in a weighed basin.

Basin + dry residue	=	29·869 gms.
Basin	=	29·622 ,,
Dry residue . . .	=	0·247 ,,

As 1000 c.cs. of the solution contains 6 gms. of extract, the 50 c.cs. evaporated will correspond to 0·3 gm. of original extract.

∴ 0·3 gm. of extract contains 0·247 gm. of total solids

$$100 \text{ gms. of the extract will contain } \frac{0{\cdot}247 \times 100}{0{\cdot}3} \text{ gms. total solids}$$

$$= 82{\cdot}3 \text{ per cent. total solids.}$$

The moisture will therefore be = 17·7 per cent.

Total Soluble Matter.—50 c.cs. of the clear filtered solution evaporated to dryness, etc.

Basin + residue of soluble matter	=	25·653 gms.
Basin	=	25·436 gms.
Residue of soluble matter . .	=	0·217 gms.

∴ 0·3 gm. of the extract contains 0·217 gm. of soluble matter

$$100 \text{ gms. will contain } \frac{0{\cdot}217 \times 100}{0{\cdot}3}$$

$$= 72{\cdot}3 \text{ per cent.}$$

The difference between the total solids and the total soluble matter will give the insoluble matter.

Therefore insoluble matter = 10·0 per cent.

Non-tannin Matter.—

Basin + residue from 50 c.cs. of detannised solution	= 32·546 gms.
Basin	= 32·522 "
Residue from 50 c.cs. of detannised solution	= 0·024 gm.
Residue from 50 c.cs. of original solution	= $\frac{6}{5}$ × 0·024 gm.
	= 0·0288 gm.

∴ 0·3 gm. of the extract contains 0·0288 gm. non-tans.

$$100 \text{ gms. will contain } \frac{100 \times 0{\cdot}0288}{0{\cdot}3}$$

$$= \underline{9{\cdot}6} \text{ per cent.}$$

Tannin.—The tannin is obtained by subtracting the soluble non-tans from the total soluble matter.

$$(72{\cdot}3 - 9{\cdot}6) = 62{\cdot}7 \text{ per cent.}$$

The results of the above analysis will be—

Tannin	62·7	per cent.
Soluble non-tans	9·6	"
Insoluble matter	10·0	"
Moisture	17·7	"
	100·0	"

Example 2.—14 gms. of a sample of sumach was extracted to 1000 c.cs. in the usual way in a Procter's extractor, and the analysis made on this solution.

Total Soluble Matter (50 c.cs.).—

Basin + dried residue	= 23·538 gms.
Basin	= 23·251 "
Weight of dried residue	= 0·287 "

Now 1000 c.cs. of the solution represents 14 gms. of sample.
∴ 50 c.cs. represent 0·7 gm.
∴ 0·7 gm. sample contain 0·287 gm. of soluble matter.

$$100 \text{ gms. will contain } \frac{0{\cdot}287 \times 100}{0{\cdot}7}$$

$$= 41{\cdot}0 \text{ per cent. total soluble matter}$$

Non-tannins.—

Basin + residue from 50 c.cs. of detannised solution	= 20·849 gms.
Basin	= 20·766 "
Residue	= 0·083 gm.
Residue from 50 c.cs. of original solution	= $\frac{6}{5}$ × 0·083
	= 0·0996 gm.

∴ 0·7 gm. of the sumach contains 0·0996 gm. of non-tannins.

$$100 \text{ gms. will contain } \frac{100 \times 0{\cdot}0996}{0{\cdot}7}$$

$$= 14{\cdot}2 \text{ per cent.}$$

Tannin.—This is obtained by subtracting the non-tannins from the total soluble matter. Thus—

$$41{\cdot}0 - 14{\cdot}2 = 26{\cdot}8 \text{ per cent.}$$

Tannin, 26·8 per cent.

Moisture.—In dealing with natural materials like sumach, the moisture can only be estimated directly and not by difference as in the case of the extract. A known amount of the material is dried at 100°–110° C. until the loss in weight is constant.

Basin + sumach	= 32·638 gms.
Basin	= 27·632 ,,
Sumach . . .	= 5·006 ,,
Basin + sumach	= 32·638 ,,
Basin + sumach after drying	= 32·002 ,,
Loss due to moisture	= 0·634 ,,
Percentage of moisture	$= \frac{100 \times 0{\cdot}634}{5{\cdot}006}$
	= 12·6 per cent.

Insoluble Matter.—This is obtained by difference. The sum of the total soluble matter and moisture is subtracted from 100·0.

$$100 - (41{\cdot}0 - 12{\cdot}6) = 46{\cdot}4 \text{ per cent.}$$

The completed analysis will be—

Tannin	26·8
Soluble non-tannins	14·2
Insoluble matter	46·4
Moisture	12·6
	100·0

Colour Measurement of the Tannin Solution.—The colour of the tannin solution is measured in terms of the red, yellow and blue units of the Lovibond tintometer through a 1 cm. cell. The colour measurement is then calculated to a basis of a 0·5 per cent. solution of tannin.

An example will show the method of calculation.

Example.—The solution as made up in the analysis of sumach given above was matched by the aid of the tintometer

in a 1 cm. cell, and the standard coloured glasses required were—

Red	1·5 units
Yellow	4·6 „

Now, according to the figures already given, this solution contains (0·287 – 0·0996) gm. of tannin per 50 c.cs. = 0·1874 gm. In other words, the solution contains 0·3748 gm. tannin per 100 c.cs. The colour of a 0·5 per cent. solution will be therefore—

$$\text{Red} \quad . \ . \ . \ . \ . \ . \quad \frac{0·5 \times 1·5}{0·3748} \text{ units} = 2·0$$

$$\text{Yellow} \quad . \ . \ . \ . \ . \quad \frac{4·6 \times 0·5}{0·3748} \quad „ \quad = 6·1$$

If any blue is found in the colour, the quantity found is deducted from both red and yellow and the blue taken as black. This deduction must be made before calculating to the 0·5 per cent. tannin basis.

Tanning Trials.— A small tanning trial carried out in the laboratory is often of value in ascertaining the colour which will be given by the tanning material when used on a large scale. For the test, a thoroughly delimed sheep grain may be used, or, for preference, a piece of delimed calf skin. The tanning is started in a weak liquor of about the same strength as the analytical solution (the solution left over from the analysis will do to start the tanning with). The liquor is gradually strengthened up by the addition of a little more of the tanning material. The trial can be conveniently carried out in a large bottle fitted into a mechanical shaker. After the pelt is tanned through, it is rinsed in warm water, slicked out on a glass plate, and hung up to dry. If necessary, it can be very slightly oiled on the grain side with a little cod oil. This will prevent any oxidation and darkening on this side.

Specific Gravity.—The specific gravity of liquid extracts should always be taken, as this serves as a guide on different barrels of the same make. The specific gravity can be determined either with a specific gravity bottle or by a hydrometer.

Other Quantitative Methods for Tannin Estimation.—A very large number of methods have been suggested for the estimation of tannin, but from the tanner's point of view they are not so satisfactory as the hide powder shake method. It will be of interest, however, to mention a few that have been proposed.

Casein Method.—This was proposed by Nierenstein,[3] and is based on the absorption of tannin by fat-free casein. 100 c.cs. of the weak tannin solution is shaken with 6 gms. of fat-free casein for 10 minutes, and then a further 3 gms. added. The liquid is filtered and the non-tannins estimated by evaporating a known volume of the detannised solution to dryness and weighing the dried residue. The total soluble matter is estimated in another portion of the solution and the tannin estimated by difference. The principle of the method is the same as the hide powder method.

Strychnine Method.—This method makes use of the fact that strychnine precipitates tannin from a solution in the form of strychnine tannate. It was introduced by Trotman and Hackford,[1] and is without doubt the most scientific and exact method that has been suggested. It is not, however, a good method for technical purposes, and is more adapted for the determination of actual tannin in a substance.

A quantity of the material to be examined is extracted with alcohol in a special designed Soxhlet apparatus. The extract containing the tannin is concentrated to 50 c.cs. and transferred to a 100 c.c. measuring flask and water added to the 100 c.c. mark. This precipitates rosins, etc. The solution is filtered and the tannin estimated in 25 c.cs. of the clear filtrate. This is placed in a 250 c.c. flask and diluted with water. 0·25 gm. of strychnine is added, previously dissolved in alcohol, and the solution diluted with an equal volume of water and cooled. After allowing to stand for a while, the solution is filtered off, and the precipitate washed, dried and weighed as strychnine tannate, $C_{21}H_{22}N_2O_2 . C_{14}H_{10}O_9$. From this the weight of tannin can be calculated. Gallic acid is not precipitated by the strychnine.

Nickel Hydroxide Method.[5]—Singh and Ghose have suggested the use of nickel hydroxide. The hydroxide used must be free from sulphates, etc.

20 gms. are used for detannising the tannin solution, and the authors state that the method is being used in India where supplies of hide powder are uncertain, and that it gives results comparing well with those obtained by the hide powder shake method.

Gawalowski[6] proposes the use of a basic copper solution.

Lead Carbonate Method—In this process the details are similar to those of the Nickel Hydroxide method (above) with the exception that in place of this latter substance lead carbonate is used. 10 gms. of the carbonate are shaken with

200 c.cs. of the tannin solution to effect detannisation. The present writer some few years ago used this method for the examination of chestnut extracts. The details as regards the strength of the solution, etc., were observed as in the official method, and 10 gms. of lead carbonate was used to detannise 100 c.cs. of the solution. Results were obtained which were decidedly encouraging. It appears that this, or a very similar method, is being used in India.[7]

Iodine Method.—The titration of tannin by means of iodine was first investigated by Jean, and has more recently been studied by Lee.[8] This latter worker carries out the determination as follows:—

5 c.cs. of the tanning solution containing not more than 1 gm. tannin per litre is measured into a stoppered bottle and 25 c.cs. of $\frac{N}{50}$ iodine solution added. The mixture is allowed to re-act for 20 minutes when the excess of iodine is titrated back with $\frac{N}{50}$ $Na_2S_2O_3$, using starch paste as internal indicator. This titration will include tannin and soluble non-tannin matters, so that the titration must be repeated on 6 c.cs. (= 5 c.cs. of original solution) of the solution detannised by the official hide powder shake method. The difference between these two titrations will give the iodine consumed by the tannin. In order to standardise the iodine solution, the latter is titrated against 5 c.cs. of a solution of gallic acid containing 1 gm. of gallic acid per litre.

Having determined the gallic acid value of the tannin present, it may be converted into tannin by multiplying by the necessary factor as given by Procter (see Table IX). This factor varies a little for different tannins.

TABLE IX

Chestnut extract		1·65
Oakwood extract		1·89
Myrobalans		1·73
Quebracho extract		1·69
Larch bark, hemlock bark		1·92
Hemlock extract, Spruce bark	2·28	2·53
Valonia, Sumach		1·55
Oak bark		1·71
Mimosa bark		1·88
Mangrove bark		1·46
Cube gambier		1·78
Gallotannic acid		1·34
Sulphite cellulose extract		8·72

From the table of comparative results given by Lee (*loc. cit.*), it would appear that the iodine method would answer

as well in many respects as the Lowenthal oxidation method (below).

Lowenthal Oxidation Method.—This method depends on the oxidising properties of potassium permanganate. The original method of Lowenthal has been considerably modified and improved by Procter and his co-workers, and the details as recommended by Procter are as follows:—

The solutions required are—

(1) *Indigo Solution.*—5 gms. of pure indigo carmine is treated with 50 gms. of concentrated H_2SO_4, and the solution made up to 1000 c.cs. with distilled water. This should be filtered.

(2) *Potassium Permanganate Solution.*—A solution of 0·5 gm. per litre is prepared. Dilute solutions of this salt do not keep well for a great length of time.

(3) *Gallic Acid Solution.*—1 gm. of the purest gallic acid is made up to a 1000 c.cs. with distilled water.

Details.—25 c.cs. of the indigo solution is carefully measured into a large white porcelain basin and diluted with about 750 c.cs. of good tap water. The permanganate is then slowly run in with constant stirring of the liquid until the blue colour is discharged, and the solution turns a pure lemon-yellow colour. Constant and rather vigorous stirring is essential. This titration is termed the indigo value.

Another 25 c.cs. of the indigo is measured out into the basin and 5 c.cs. of the gallic acid solution added. The liquid is then titrated with the permanganate solution as before.

The difference between this titration and the indigo titration gives the permanganate required by the 5 c.cs. of gallic acid solution.

From this figure the gallic acid value of 1 c.c. of the permanganate can be calculated.

Example.—

25 c.cs. of indigo solution + 5 c.cs. of gallic acid solution	= 47·8 c.cs.
25 c.cs. of indigo solution alone	= 28·2 c.cs.
5 c.cs. of gallic acid solution	= 19·6 c.cs.
Now 5 c.cs. of the gallic acid solution contain	= 0·005 gm. gallic acid
∴ 19·6 c.cs. of permanganate solution	= 0·005 gm. gallic acid
and 1 c.c. of permanganate	= 0·000255 gm. gallic acid

So far, therefore, the permanganate has been standardised.

25 c.cs. of indigo and 5 c.cs. of the filtered tannin solution are measured in the basin and titrated with permanganate and the volume required noted.

This volume represents the indigo solution added, and the non-tannins and tannins in 5 c.cs. of the liquor.

The non-tannins must now be determined. For detannising lightly chromed hide powder will be found most convenient. 7 gms. of the dry chromed powder and a little kaolin are added to 100 c.cs. of the solution, and the whole shaken in a mechanical shaker for 15 minutes. It is then filtered, and 5 c.cs. of the clear filtrate, together with 25 c.cs. of indigo, titrated with permanganate solution. This titration will correspond to the non-tannins and indigo only, so that the permanganate corresponding to the tannin is obtained by difference.

Example.—

5 c.cs. liquor + 25 c.cs. indigo . . .	= 39·2 c.cs. $KMnO_4$
5 c.cs. detannised liquor = 25 c.cs. indigo solution	= 30·2 c.cs.
∴ tannin in 5 c.cs. of liquor	= 9·0 c.cs.

Now 1 c.c. $KMnO_4$ is equivalent to 0·000255 gm. gallic acid
∴ 9·0 c.cs. „ „ 0·0002295 „ „

5 c.cs. of solution contains tannin equivalent to 0·002295 gm. gallic acid.

100 c.cs. of solution contains tannin equivalent to 0·0459 gm. gallic acid.

To convert the gallic acid value into tannin it is necessary to multiply by the factor (which will vary for different materials) as indicated on p. 136, Table IX.

The tannin in any material can be determined by this method, a known amount being extracted or dissolved in water and the solution made up to a definite volume.

The method is useful when dealing with a large number of liquors in process control work, but for the examination of tanning materials the hide powder method is to be preferred. The diluting of strong liquors, etc., should be so regulated that 5 c.cs. of the filtered solution should not require more than 50 c.cs. of the permanganate.

Direct Determination of Tannin in Quebracho.—On more than one occasion attempts have been made to use the formaldehyde test (see p. 111) in a quantitative manner. Tranke,[9] by so doing, estimates directly the tannin in quebracho. 50 c.cs. of the solution (20 gms. bark extracted to 1000 c.cs.) is diluted with 100 c.cs. of water and 50 c.cs. of

40 per cent. formalin added. The solution is boiled and 25 c.cs. of 25 per cent. HCl added. The liquid is allowed to stand for 30 minutes and the precipitate then filtered. This is washed with water, alcohol, and finally ether. It is then dried at 110° C. and weighed. The weight of the precipitate multiplied by the factor 0·9834 = quebracho-tannic acid.

Microscopical Examination of Tanning Materials.—The microscopical examination of certain tanning materials, especially in the case of sumach, gives very useful information. Sumach is liable to be adulterated with inferior materials such as pistica lentiscus, tamarix, etc., which can only be satisfactorily detected by means of the microscope.

It is best examined according to the methods of Lamb, Harrison[10] and Priestman,[11] whose original papers should be consulted, as they include valuable photographs of the various adulterants.

The ash of sumach is generally about 6·5–7 per cent., and if higher should be examined for sand, etc. Turnbull employs the following method for the estimation of extraneous matter in sumach:—20 gms. of the sample is shaken in a separating funnel with 100–150 c.cs. of carbon tetrachloride. The mixture is allowed to stand overnight when the mineral matter will have settled to the bottom of the funnel. This can be taken out, dried and weighed. The presence of metallic iron in sumach is also of importance, and in a properly prepared material should be absent. The quantity of iron present can be determined by passing a strong electro-magnet through a known weight of the sample and the iron collected and weighed (Trotman).

A general article on the examination of tannin extracts has been written by Grasser,[13] while Brumwell[14] has gone more fully into the examination of Gambier.

The composition of a number of tanning materials are given in the table on pp. 140–141.

Sulphited Extracts.—The estimation of bi-sulphites in a sulphited extract may be carried according to the following method[15]:—

5 gms. of the extract is weighed out and dissolved in about 100 c.cs. of distilled water. The solution is boiled and 10 c.cs. of 10 per cent. HCl added. The sulphates are then precipitated with an excess of hot solution of barium chloride. The barium sulphate is filtered, washed well with hot distilled water, dried, ignited and weighed. Another 5 gms. of the extract is dissolved in a little warm water, and the bi-sulphites

TABLE X

COMPOSITION OF TANNING MATERIALS

		Tannin.	Non-tannin.	Insoluble.	Moisture.	Authority.	Reference.
Wattle bark (Australian)	Acacia pycnantha (No. 1 special)	49·5	9·4	29·0	11·2	Blockey	J.S.C.I., 1902, p. 159.
,, ,, ,,	A. decurrens var. mollissima	38·3	4·4	45·2	11·1	,,	,, ,, ,,
,, ,, ,,	A. dealbata	12·2	4·3	71·9	11·6	,,	,, ,, ,,
,, ,, ,,	A. decurrens var. normalis	41·4	7·0	39·2	11·5	,,	,, ,, ,,
,, ,, (African)	A. decurrens var. mollissima	37·8	9·3	43·4	9·5	Imperial Institute	Bull., 1908, p. 165.
,, ,, ,,	A. horrida	18·3	8·3	62·4	11·0	,, ,,	,, ,, ,,
,, ,, ,,	A. dealbata	17·42	6·54	64·89	11·15	,, ,,	,, ,, ,,
Valonia (Smyrna)	Quercus ægilops (cup)	30·99	12·79	44·12	12·10	Parker and Leach	J.S.C.I., 1903, p. 1184.
,, ,,	,, ,, (beard)	43·61	14·45	29·93	12·01	,, ,,	,, ,, ,,
,, (Greek)	,, ,, (cup)	27·37	12·92	47·71	12·00	,, ,,	,, ,, ,,
,, ,,	,, ,, (beard)	41·03	13·96	33·01	12·00	,, ,,	,, ,, ,,
Myrobalans	Terminalia chebula.						
,,	,, picked Bhimley	33·0	13·1	41·7	12·0	Parker and Blockey	J.S.C.I., 1903, p. 1183.
,,	,, No. 1 ,,	38·4	16·1	33·5	12·0	,, ,,	,, ,, ,,
,,	,, No. 2 ,,	35·2	14·2	38·6	12·0	,, ,,	,, ,, ,,
,,	,, picked Rajpore	32·2	13·0	42·8	12·0	,, ,,	,, ,, ,,
,,	,, No. 1 ,,	35·4	12·1	40·5	12·0	,, ,,	,, ,, ,,
,,	,, No. 2 ,,	27·6	12·7	47·7	12·0	,, ,,	,, ,, ,,
,,	,, picked Jubblepore	28·9	12·7	46·4	12·0	,, ,,	,, ,, ,,
,,	,, No. 1 ,,	36·5	14·4	37·1	12·0	,, ,,	,, ,, ,,
,,	,, No. 2 ,,	27·3	14·1	46·6	12·0	,, ,,	,, ,, ,,

Sal (leaves and twigs)	Shorea robusta	22·84	34·58	42·58	0·0	Fraymouth and Pilgrim	*Bull.*, No. 1. Escoit Fact.
Sal bark	,, ,,	9·12	7·66	83·22	0·0	,, ,,	,, ,, ,,
Divi-divi pods	Cæsalpinia coriaria	44·52	23·57	31·91	0·0	,, ,,	,, ,, ,,
Tunwad bark	Cassia auriculata	19·51	14·69	65·80	0·0	,, ,,	,, ,, ,,
Mallet bark	Eucalyptus occidentalis	42·0	8·0	35·5	14·5	Imperial Institute	*Bull.*, 1908, p. 318.
Guara (Cascalotte)	—	46·2	25·8	19·0	9·0	Callan	*J.S.C.I.*, 1915, p. 645.
,, extract	—	41·7	30·0	11·0	17·3	,,	,, ,, ,,
Sumach	Rhus coriaria	27·0	16·0	45·0	12·0	Author	—
Chestnut extract	(liquid)	26·8	15·0	1·0	57·2	,,	Vary from 23–30% tan.
,, ,,	(solid)	53·0	31·0	2·0	14·0	,,	Vary from 50–60% tan.
Mimosa extract	(liquid)	36·0	12·0	0·2	51·8	,,	—
Quebracho extract	(solid)	65·0	7·0	10·0	18·0	,,	—
,, ,,	(liquid)	32·0	9·0	3·0	56·0	,,	—
Myrobalans ,,	(solid)	51·0	29·0	7·0	13·0	,,	—
Mangrove bark (Australian)	Rhizophora mucronata	33·09	10·60	43·80	12·5	Coombs and Alcock	*Leather World*, 1912, p. 850, *et seq.*
,, ,, ,,	Bruguera gymnorrihiza	29·12	8·97	49·41	12·5	,, ,,	,, ,, ,,
,, ,, ,,	Ceriops condolleana	30·47	11·36	45·66	12·5	,, ,,	,, ,, ,,
Oak bark	Quercus robur, etc.	12·5	6·0	67·5	14·0	Author	—
Valonia extract	—	68.0	24·3	0·2	7·5	Paessler	*C.T.*, 1907, p. 273.
Lentisco	Pistacia lentiscus	14·0	27·0	45·0	14·0	Average figures	—
Tamarix	Tamarix africana	10·0	24·0	52·0	14·0	,, ,,	—
Quebracho wood	Quebrachia lorentzii	20·0	3·0	61·0	16·0	,, ,,	—

oxidised to sulphates by the addition of 10–15 c.cs. of bromine water.

$$Br_2 + NaHSO_3 + H_2O = 2HBr + NaHSO_4$$

The solution is allowed to stand for a short time and then 10 c.cs. of 10 per cent. HCl added. The excess of bromine is expelled by boiling, and the total sulphate estimated by adding barium chloride solution in the usual way. The additional $BaSO_4$ found after oxidation multiplied by the factor 0·4459 will give the weight of $NaHSO_3$ in 5 gms. of the sample.

If required, the bi-sulphites present can be calculated as SO_2 by multiplying the weight of $BaSO_4$ by the factor 0·2744.

REFERENCES

[1] *Coll.*, 1907, p. 14, *et seq.*
[2] *J.S.C.I.*, 1904, p. 458.
[3] *Chem. Zeit.*, 1911, p. 31.
[4] *J.S.C.I.*, 1905, No. 21.
[5] *Ibid.*, 1911, p. 936 (cf. *J.S.C.I.*, 1916, p. 159; *Coll.* (London Edition), 1916, p. 165.
[6] *Abst. Coll.* (London Edition), 1916, p. 47.
[7] *Bull.*, No. 1 Escoit Tannin Research Factory, 1918.
[8] *Jour. Soc. Leather Trades Chem.*, 1919, p. 8.
[9] *Abst. Jour. Amer. Leather Chem. Assoc.*, 1907, p. 145
[10] *J. Soc. Dyers Cols.*, 1899, No. 3.
[11] *J.S.C.I.*, 1905, p. 231.
[12] *Coll.*, 1913, p. 138
[13] *Ibid.*, 1911, p. 349.
[14] *Ibid.*, p. 382.
[15] *Leather* (now *Leather World*), 1911, p. 523

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CHAPTER XVI

TAN LIQUORS

As a rule the examination of a tannery liquor involves the determination of the amount of tannin present, and the acidity of the liquor.

The tannin may be determined either by the hide powder shake method, or for comparative purposes, where a large number have to be periodically analysed by the Lowenthal permanganate method. The liquor will, in the majority of cases, have to be diluted so as not to contain not more than 4·5 gms. per litre of tanning matters. This dilution can only be made as the result of a preliminary trial. The barkometer strength is of little use as a guide to the dilution necessary owing to the varying quantities of soluble non-tanning matter present in the liquors.

A most important determination is the acidity, and even at the present time, in spite of the large amount of work which has been done on the subject, there exists no accurate method which could be applied to liquors in general. However, a brief mention of the more important processes which have been suggested will be of interest.

Yocum, Faust and Riker's Method.—50 c.cs. of gelatine solution and 15 c.cs. of a 2 per cent. solution of gum arabic are added to 15 c.cs. of the liquor and the whole made up to 200 c.cs. in a graduated flask and well shaken. 5 gms. of kaolin is added and the solution filtered. 40 c.cs. of the clear filtrate is titrated with $\frac{N}{10}$NaOH, using hæmatine as indicator. This gives the acidity of 3 c.cs. of the original liquor. For control purposes this may be calculated to c.cs. of $\frac{N}{10}$NaOH per 100 c.cs. of liquor, or expressed as acetic acid.

Hoppenstedt's Method.[1]—In this method the tannin is first precipitated by quinine, and the acidity of the detannised

solution titrated with alkali. The quinine solution used is prepared by dissolving 15 gms. of pure quinine in 110 c.cs. of 95 per cent. alcohol, and adding slowly 90 c.cs. of water.

50 c.c. of the liquor is measured into a 500 c.c. flask and made up to the mark with distilled water. To 200 c.cs. of this solution is added 20 c.cs. of the quinine solution, and the whole well shaken and filtered. 100 c.cs. of the filtrate is titrated with $\frac{N}{10}$NaOH, using phenol phthalein as indicator. The number of c.cs. required multiplied by 0·066 will give the percentage of acidity in terms of acetic acid.

Lead Oxide Method.—The use of lead oxide for the determination of the acidity of liquors was first suggested by Bennett,[2] and for details concerning this method the original paper should be consulted.

Lime Water Method.—This is the method most widely used in practice, and was introduced by Procter. 10 c.cs. of the filtered liquor is titrated with a clear saturated solution of lime water until the solution appears cloudy when viewed over a slip of printed paper. If the beaker is held about 2 cms. from the surface of the paper, the endpoint will be readily observed. By this method the weak acids present are neutralised by the lime water, a slight excess of which causes the precipitation of the insoluble calcium salt of the tannin.

The number of c.cs. of saturated lime water required by 10 c.cs. of the liquor is termed the degrees of acidity of the liquor. This reading gives a direct measure of the lime neutralising capacity of the liquor. If preferred, the lime water may be standardised against $\frac{N}{10}$ acid, and from the factor obtained, the c cs. of lime water can be converted into terms of $\frac{N}{10}$ acid. Further, from this figure the acidity can be calculated into acetic acid.

Many other methods have been suggested, based mainly on the use of various indicators. A number of these were further investigated by Procter and Seymour-Jones.[3] To illustrate the different readings obtained by using various indicators, the following results are quoted from Procter and Seymour-Jones (*loc. cit.*).

In Terms of c.cs. $\frac{N}{10}$ Alkali per 25 c.cs. of Liquor.

	Lime water.	Hæmatine.	Congo red.
Oak liquor	8·0 c.cs.	16·0 c.cs.	5·9 c.cs.
Mixed valonia liquor . . .	9·2 c.cs.	14·5 c.cs.	10·7 c.cs.

In the above experiments the hæmatine and congo red were used as external indicators. In concluding their paper, the authors consider that the hæmatine represents the total acidity, the congo red the plumping power of the liquor, and the lime water titration the lime dissolving power.

Electro-metric Method.—An electro-metric method for determining the acidity of a liquor has been devised by Sand and Law.[4]

Sulphuric Acid in Liquors.—The following method for determining the sulphuric acid in liquor was suggested by Parker and Payne[5]:—

10 c.cs. of the liquor is treated with 90 c.cs. of absolute alcohol well mixed and allowed to stand for some time. It is then filtered and the sulphuric acid in the filtrate estimated as $BaSO_4$ in the usual way. The alcohol should be first expelled, the residue diluted, HCl added, followed by a hot solution of barium chloride.

As will be seen, the method is based on the insolubility of sulphates and the solubility of sulphuric acid in alcohol.

Dissolved Hide Substance.- The total nitrogen is estimated by the Kjeldahl method (see p. 21) and from this figure the hide substance calculated. This will also include any nitrogenous matters dissolved out from the tanning materials, but as a rule this will be very small indeed. (In this connection the quantity of nitrogenous matter in various tanning materials has been investigated by Bennett.[6])

Another rapid method by Parker and Casaburi is as follows:—250 c.cs. of the liquor is measured into a 500 c.c. measuring glass, and neutralised by adding caustic soda solution. An excess of a saturated salt solution is then added together with a convenient quantity of solid salt. The hide substance salted out rises to the surface of the solution and forms a spongy mass. This is collected, dried and weighed. This is a method which can be well adapted for a ready works method. The precipitate from a number of liquors are allowed to settle for a definite length of time and the volume read off in c.cs. Using the same liquors, the

total nitrogen by Kjeldahl's method is determined. From a series of such determinations, the per cent. of hide substance corresponding to 1 c.c. of the measuring jar can be ascertained. This factor can then be used for reading direct the percentage of hide substance in the liquor. Standard time for settling, etc., would have to be adopted.

REFERENCES

[1] *Jour. Amer. Leather Chem. Assoc.*, 1906, p. 192.
[2] *J.S.C.I.*, 1907, No. 22.
[3] *Coll.*, 1911, p. 219, *et seq.*
[4] *Ibid.*, 1911, p. 150 *et seq.*
[5] *Ibid.*, 1904, p. 670.
[6] *Ibid.*, 1916, p. 1.

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CHAPTER XVII

LEATHER ANALYSIS

Vegetable Tanned Leather.—According to the details laid down by the Society of Leather Trades' Chemists,[1] the complete analysis of sole leather should comprise the following determinations :—

Moisture as received.
Oil and fat.
Water soluble matter at 45° C.
Ash of soluble matter.
Glucose.
Other organic matter (by difference)
Insoluble leather substance.
Hide substance by Kjeldahl.
Fixed tanning matters.
Ash of insoluble leather substance.

The above figures are afterwards calculated to a moisture content of 14·0 per cent., thus making all leather analyses comparable.

Preparation of the Sample.—The preparation of the sample is a very important matter, and the method proposed by the above Society is, without doubt, the best. This is to plane or spokeshave the sample into very thin shavings. The material should never be ground in a mill, as a certain amount of "burning" takes place, with the result that certain constituents are affected. Thus, Godel[2] has shown that even if the leather is heavily rasped the water soluble matter will be increased. The present author has noticed that if a leather is ground in a mill the water extract is nearly always darker in colour than that obtained when the sample is planed with an ordinary carpenter's plane.

Moisture.—5 gms. of the sample, prepared as suggested above, is weighed into a basin and dried at 98°–100° C. in the vacuum oven for two hours. The loss in weight is taken as moisture. Instead of the vacuum oven a steam oven can

be used, in which case the drying is continued until the loss in weight is constant. Wilkinson[3] does not consider two hours' drying in the vacuum oven sufficient, and maintains that even by the use of this apparatus the sample should be dried to constant weight. Nicolardot[1] removes the grease from the leather before drying. The sample is de-greased and then dried for 3–4 hours at 100°–110° C. The amount of grease extracted is allowed for. The results are said to be 2·0 per cent. higher than those obtained by drying in vacuo for 48 hours.

Hide Substance.—The hide substance is determined by the Kjeldahl method (see p. 21), using the quantity already suggested, or, if preferred, 0·6–0·7 gm. of leather without any subsequent dilution of the solution. Bennett[5] has proposed the use of the Ronchèse method, the details for which are as follows:—

0·4–0·5 gm. of leather is heated with 15 c.cs. of pure nitrogen free sulphuric acid until perfectly clear and free from unoxidised organic matter. The acid liquid is diluted with distilled water and made exactly neutral by adding, first a 50 per cent. solution of NaOH, and finally $\frac{N}{10}$ NaOH, a few drops of phenol phthalein being added to the solution. When neutral, 25 c.cs. of neutral 40 per cent. formalin is added. The following reaction takes place:—

$$2(NH_4)_2SO_4 + 6H.CHO = 2H_2SO_4 + N(CH_2.N:CH_2)_3 + 6H_2O$$

As the hexamethylene tetramine is neutral to phenol phthalein, the sulphuric acid liberated according to the above equation may be titrated direct with $\frac{N}{10}$ NaOH, using this indicator. Some comparative results obtained by Bennett (*loc. cit.*) are given below:—

	H.CHO method	Kjeldahl method
Sample 1	12·2 per cent. N	12·[illegible] per cent. N
Sample 2	12·5 ,, ,,	12·48 ,, ,,
Sample 3	12·2 ,, ,,	12·2 ,, ,,
Sample 4	14·7 ,, ,,	14·68 ,, ,,

These seem very encouraging results although some chemists do not favour the method.

Fat and Oil.—20 gms. of the leather is extracted with petrol ether, B.P. 40°–60° C., for 6 hours. The ether is

evaporated and he residue of fat dried in the steam oven to approximate constant weight. The extracted fat may then be examined by the methods given in Chap. XIII. and the nature of the material ascertained. Apart from petrol ether, many solvents have been suggested for the extraction of the fat.

Wilson and Kern[6] show that petrol ether is not a suitable solvent owing to the insolubility in this liquid of oxidised and hydroxylated oils. They recommend the use of a mixture of equal volumes of ethyl ether and carbon tetra-chloride. Levi and Orthmann,[7] however, do not favour this modification as they find that the mixture extracts considerable quantities of non-fatty substances from vegetable tanned leather, and at the same time is not considered entirely suitable for chrome tanned material. Quite recently, the Sole Leather Analysis Committee of the American Leather Chemists' Association[8] have favoured the use of chloroform for the purpose. There appears to be room for further work on this question, as owing to the mixed nature of greases used there is no general solvent which can be applied to all leathers.

The method for estimating fat without the use of the Soxhlet apparatus is described by Levi and Orthmann,[9] and has been used by the present author with good results. 10 gms. of the prepared sample is transferred to a glass stoppered bottle and treated with 200 c.cs. of petrol ether. The mixture is allowed to stand for 48 hours with frequent shakings. 100 c.cs. of the etheral solution is pipetted off into a weighed flask and the solvent distilled off. The residue of fat is then dried and weighed. This gives the quantity of fat in 5 gms. of original leather.

Water Soluble Matter.—The residue of fat-free leather obtained from the extraction of 20 gms. is freed from the last trace of petrol ether by exposure to the air and then transferred to a Procter's extractor (the sand in this case should be omitted). The leather is covered with a convenient quantity of distilled water and allowed to soak overnight. The leather is then extracted at a temperature of 45° C. until 1000 c.cs. has been collected. The aqueous extract is then cooled under the tap and made up to 1000 c.cs. with distilled water. The solution is filtered through a pleated filter paper, rejecting the first 500 c.cs. of filtrate, and then 50 c.cs. collected and evaporated to dryness in a weighed dish. The residue is then dried in the steam or vacuum oven until constant in weight. This gives the soluble matter in 1 gm. of original leather. If necessary, the uncombined

tannin in the water soluble matter can be estimated by the hide powder shake method (see p. 124). The difference between this and the total water soluble matter will give the non-tannin substances.

Sugars.—The total sugars estimated as glucose is carried out on a portion of the aqueous extract. 200 c.cs. of the aqueous extract is treated with 20 c.cs. of a solution of basic lead acetate, well stirred and allowed to stand for a quarter of an hour. The solution is then filtered and the filtrate treated with solid anhydrous sodium carbonate. This is to precipitate the excess of lead, and is added as long as any precipitate of lead carbonate is formed. The liquid is again filtered and made neutral with HCl. Non-reducing sugars are next inverted by heating 110 c.cs. of the filtrate (= 100 c.cs. of original solution) with about 8 10 c.cs. of HCl on the water bath for about an hour, using a reflux condenser to avoid evaporation. After invertion, the liquid is cooled down and neutralised with a strong solution of NaOH. The neutralised liquid is now added to a mixture of 30 c.cs. each of the Fehling's solution (for preparation of which see below) and heated to the boil. It is then heated on the water bath for 30 minutes, at the end of which time the cuprous oxide is filtered through a weighed Gooch crucible containing a thin layer of asbestos. It is washed first with hot water and then alcohol, and finally dried in the oven and weighed. The cuprous oxide found is converted into its equivalent of copper by multiplying by the factor 0·8883, and from this latter figure the weight of glucose can be ascertained from the table (see Table XI.).

TABLE XI

Munson and Walker's Table

(Bulletin 107, Revised, Bureau of Chemistry, U.S., p. 243.)
(Expressed in milligrams.)

Copper (Cu).	Dextrose (d-glucose)	Copper (Cu)	Dextrose (d-glucose)	Copper (Cu).	Dextrose (d-glucose)
8·9	4·0	40·0	19·1	71·1	34·4
9·8	4·5	40·9	19·6	71·9	34·9
10·7	4·9	41·7	20·0	72·8	35·3
11·5	5·3	42·6	20·4	73·7	35·8
12·4	5·7	43·5	20·9	74·6	36·2
13·3	6·2	44·4	21·3	75·5	36·7
14·2	6·6	45·3	21·7	76·4	37·1
15·1	7·0	46·2	22·2	77·3	37·5
16·0	7·5	47·1	22·6	78·2	38·0
16·9	7·9	48·0	23·0	79·1	38·4
17·8	8·3	48·9	23·5	79·9	38·9
18·7	8·7	49·7	23·9	80·8	39·3
19·5	9·2	50·6	24·3	81·7	39·8
20·4	9·6	51·5	24·8	82·6	40·2
21·3	10·0	52·4	25·2	83·5	40·6
22·2	10·5	53·3	25·6	84·4	41·1
23·1	10·9	54·2	26·1	85·3	41·5
24·0	[illegible]	55·1	26·5	86·2	42·0
24·9	11·8	56·0	27·0	87·1	42·4
25·8	12·2	56·8	27·4	87·9	42·9
26·6	12·6	57·7	27·8	88·8	43·3
27·5	13·1	58·6	28·3	89·7	43·8
28·4	13·5	59·5	28·7	90·6	44·2
29·3	13·9	60·4	29·2	91·5	44·7
30·2	14·3	61·3	29·6	92·4	45·1
31·1	14·8	62·2	30·0	93·3	45·5
32·0	15·2	63·1	30·5	94·2	46·0
32·9	15·6	64·0	30·9	95·0	46·4
33·8	16·1	64·8	31·4	95·9	46·9
34·6	16·5	65·7	31·8	96·8	47·3
35·5	16·9	66·6	32·2	97·7	47·8
36·4	17·4	67·5	32·7	98·6	48·2
37·3	17·8	68·4	33·1	99·5	48·7
38·2	18·2	69·3	33·6	100·4	49·1
39·1	18·7	70·2	34·0	101·3	49·6

TABLE XI—*continued*

Copper (Cu).	Dextrose (*d*-glucose).	Copper (Cu)	Dextrose (*d*-glucose).	Copper (Cu).	Dextrose (*d*-glucose).
102·2	50·0	137·7	68·2	173·2	86·7
103·0	50·5	138·6	68·6	174·1	87·1
103·9	50·9	139·5	69·1	175·0	87·6
104·8	51·4	140·3	69·5	175·9	88·1
105·7	51·8	141·2	70·0	176·8	88·5
106·6	52·3	142·1	70·4	177·7	89·0
107·5	52·7	143·0	70·9	178·5	89·5
108·4	53·2	143·9	71·4	179·4	89·9
109 3	53·6	144·8	71·8	180·3	90·4
110·1	54·1	145·7	72·3	181·2	90·9
111·0	54·5	146 6	72·8	182·1	91·4
111·9	55·0	147·5	73·2	183·0	91·8
112·8	55·4	148·3	73·7	183·9	92·3
113·7	55·9	149·2	74·1	184·8	92·8
114·6	56·3	150·1	74·6	185·6	93·2
115·5	56·8	151 0	75·1	186 5	93·7
116·4	57·2	151 9	75·5	187·4	94·2
117·3	57·7	152·8	76·0	188 3	94·6
118·1	58·1	153·7	76·4	189·2	95·1
119·0	58·6	154 6	76·9	190·1	95·6
119·9	59·0	155 5	77·4	191·0	96·1
120·8	59·5	156·3	77·8	191·9	96·5
121·7	60·0	157·2	78·3	192·8	97·0
122·6	60·4	158·1	78·8	193·6	97·5
123·5	60·9	159·0	79·2	194·5	98·0
124 4	61·3	159·9	79·7	195·4	98·4
125·2	61·8	160·8	80·1	196·3	98·9
126·1	62·2	161·7	80·6	197·2	99·4
127·0	62·7	162·6	81·1	198·1	99·9
127·9	63·1	163·4	81·5	199·0	100 3
128·8	63·6	164·3	82·0	199·9	100·8
129·7	64·0	165·2	82·5	200·7	101·3
130·6	64·5	166·1	82·9	201·6	101·8
131·5	65·0	167 0	83·4	202·5	102·2
132·4	65·4	167·9	83·9	203·4	102·7
133·2	65·9	168·8	84·3	204·3	103·2
134·1	66·3	169·7	84·8	205·2	103·7
135·0	66·8	170·5	85·3	206·1	104·1
135·9	67·2	171·4	85·7	207·0	104·6
136·8	67·7	172·3	86·2	207·9	105·1

TABLE XI—*continued*

Copper (Cu).	Dextrose (*d*-glucose).	Copper (Cu).	Dextrose (*d*-glucose).	Copper (Cu).	Dextrose (*d*-glucose).
208·7	105·6	244·3	124·9	279·8	144·7
209·6	106·0	245·2	125·4	280·7	145·2
210·5	106·5	246·1	125·9	281·6	145·7
211·4	107·0	246·9	126·4	282·5	146·2
212·3	107·5	247·8	126·9	283·4	146·7
213·2	108·0	248·7	127·3	284·2	147·2
214·1	108·4	249·6	127·8	285·1	147·7
215·0	108·9	250·5	128·3	286·0	148·2
215·8	109·4	251·4	128·8	286·9	148·7
216·7	109·9	252·3	129·3	287·8	149·2
217·6	110·4	253·2	129·8	288·7	149·7
218·5	110·8	254·0	130·3	289·6	150·2
219·4	111·3	254·9	130·8	290·5	150·7
220·3	111·8	255·8	131·3	291·4	151·2
221·2	112·3	256·7	131·8	292·2	151·7
222·1	112·8	257·6	132·3	293·1	152·2
223·0	113·2	258·5	132·7	294·0	152·7
223·8	113·7	259·4	133·2	294·9	153·2
224·7	114·2	260·3	133·7	295·8	153·7
225·6	114·7	261·2	134·2	296·7	154·2
226·5	115·2	262·0	134·7	297·6	154·7
227·4	115·7	262·9	135·2	298·5	155·2
228·3	116·1	263·8	135·7	299·3	155·8
229·2	116·6	264·7	136·2	300·2	156·3
230·1	117·1	265·6	136·7	301·1	156·8
231·0	117·6	266·5	137·2	302·0	157·3
231·8	118·1	267·4	137·7	302·9	157·8
232·7	118·6	268·3	138·2	303·8	158·3
233·6	119·0	269·1	138·7	304·7	158·8
234·5	119·5	270·0	139·2	305·6	159·3
235·4	120·0	270·9	139·7	306·5	159·8
236·3	120·5	271·8	140·2	307·3	160·3
237·2	121·0	272·7	140·7	308·2	160·8
238·1	121·5	273·6	141·2	309·1	161·4
238·9	122·0	274·5	141·7	310·0	161·9
239·8	122·5	275·4	142·2	310·9	162·4
240·7	122·9	276·3	142·7	311·8	162·9
241·6	123·4	277·1	143·2	312·7	163·4
242·5	123·9	278·0	143·7	313·6	163·9
243·4	124·4	278·9	144·2	314·4	164·4

TABLE XI—*continued*

Copper (Cu).	Dextrose (*d*-glucose).	Copper (Cu).	Dextrose (*d*-glucose)	Copper (Cu).	Dextrose (*d*-glucose).
315·3	164·9	350·9	185·7	386·4	207·1
316·2	165·4	351·8	186·2	387·3	207·6
317·1	166·0	352·6	186·8	388·2	208·2
318·0	166·5	353·5	187·3	389·1	208·7
318·9	167·0	354·4	187·8	390·0	209·2
319·8	167·5	355·3	188·4	390·8	209·8
320·7	168·0	356·2	188·9	391·7	210·3
321·6	168·5	357·1	189·4	392·6	210·9
322·4	169·0	358·0	189·9	393·5	211·4
323·3	169·6	358·9	190·5	394·4	212·0
324·2	170·1	359·7	191·0	395·3	212·5
325·1	170·6	360·6	191·5	396·2	213·1
326·0	171·1	361·5	192·1	397·1	213·6
326·9	171·6	362·4	192·6	397·9	214·1
327·8	172·1	363·3	193·1	398·8	214·7
328·7	172·7	364·2	193·7	399·7	215·2
329·5	173·2	365·1	194·2	400·6	215·8
330·4	173·7	366·0	194·7	401·5	216·3
331·3	174·2	366·9	195·2	402·4	216·9
332·2	174·7	367·7	195·8	403·3	217·4
333·1	175·3	368·6	196·3	404·2	218·0
334·0	175·8	369·5	196·8	405·1	218·5
334·9	176·3	370·4	197·4	405·9	219·1
335·8	176·8	371·3	197·9	406·8	219·6
336·7	177·3	372·2	198·4	407·7	220·2
337·5	177·9	373·1	199·0	408·6	220·7
338·4	178·4	374·0	199·5	409·5	221·3
339·3	178·9	374·8	200·1	410·4	221·8
340·2	179·4	375·7	200·6	411·3	222·4
341·1	180·0	376·6	201·1	412·2	222·9
342·0	180·5	377·5	201·7	413·0	223·5
342·9	181·0	378·4	202·2	413·9	224·0
343·8	181·5	379·3	202·8	414·8	224·6
344·6	182·0	380·2	203·3	415·7	225·1
345·5	182·6	381·1	203·8	416·6	225·7
346·4	183·1	382·0	204·4	417·5	226·2
347·3	183·6	382·8	204·9	418·4	226·8
348·2	184·1	383·7	205·5	419·3	227·4
349·1	184·7	384·6	206·0	420·2	227·9
350·0	185·2	385·5	206·5	421·0	228·5

TABLE XI—*continued*

Copper (Cu)	Dextrose (*d*-glucose).	Copper (Cu).	Dextrose (*d*-glucose).	Copper (Cu).	Dextrose (*d*-glucose).
421·9	229·0	426·4	231·8	430·8	234·6
422·8	229·6	427·3	232·4	431·7	235·2
423·7	230·1	428·1	232·9	432·6	235·7
424·6	230·7	429·0	233·5	433·5	236·3
425·5	231·3	429·9	234·1	434·4	236·9
				435·3	237·4

The basic lead acetate used in the above method is prepared as follows:—

300 gms. of pure normal lead acetate and 100 gms. of litharge are mixed together and made into a thick paste with distilled water. The mass is heated on the water bath until the reddish colour of the litharge disappears and the mass becomes almost white. It is then diluted to 1000 c.cs. and filtered.

The Fehling's solution should be made up in two separate solutions.

(*a*) 170 gms. of Rochelle salt (potassium sodium tartrate) and 125 gms. of pure caustic potash are dissolved in water and the solution made up to 500 c.cs.

(*b*) 34·6 gms. of pure copper sulphate is dissolved in distilled water and three or four drops of concentrated H_2SO_4 added. The solution is then made up to 500 c.cs. with distilled water. Equal volumes of these two solutions are mixed immediately before use.

In the American Official method for the estimation of glucose, the solution is detannised with a solution of normal lead acetate, but Parker and Blockey[10] have shown this to be inefficient for the purpose, and recommend the basic acetate as described above.

Various volumetric methods have been suggested for estimating the amount of copper precipitated instead of weighing it in the form of Cu_2O. Bennett[11] suggests transferring the precipitate of Cu_2O to a solution of ferric sulphate and estimating the amount of iron reduced to the ferrous condition by means of $\frac{N}{10}$ potassium permanganate solution. Appelius and Schmidt[12] have published the following procedure:—

A blank determination is first carried out with the

Fehling's solution. 15 c.cs. of each solution are mixed and diluted with 45 c.cs. of water. This is added to 300 c.cs. of water and 10 c.cs. of a KI solution (80 gms. in 250 c.cs. water) and 15 c.cs. of dilute H_2SO_4 (1 part conc. acid to 2 parts water). The liberated iodine is then titrated with $\frac{N}{10}$ $Na_2S_2O_3$ using starch paste as indicator. This gives the total copper in the volume of Fehling's solution taken. For the actual determination, 15 c.cs. each of the Fehling's solution, 35 c.cs. of water and a known volume of the detannised solution are used. The mixture is heated on the water bath as usual and then quickly cooled. It is then washed, without filtering, into a flask containing 10 c.cs. of the KI solution and 15 c.cs. of the dilute H_2SO_4. The iodine is titrated as in the blank experiment above. The difference between the latter titration and the former gives the volume of $\frac{N}{10}$ $Na_2S_2O_3$ corresponding to the copper reduced by the glucose—

$$1 \text{ c.c. } \frac{N}{10} Na_2S_2O_3 = 0{\cdot}00636 \text{ gm. Cu}$$

From the weight of copper the corresponding amount glucose may be ascertained from the table already given.

Total Ash.—5 gms. of the leather is ignited in a platinum dish and the ash weighed in the usual way. As a rule the ash of a good vegetable tanned leather will not exceed 1·5–2·0 per cent. The most likely adulterants will be magnesium sulphate and barium sulphate. Sodium sulphate may also be found.

Estimation of Barium.—5 gms. of the leather is ignited in a porcelain crucible (not platinum if barium is suspected), and the ash cooled and mixed with 3–4 gms. of fusion mixture consisting of the carbonates of sodium and potassium mixed in molecular proportions. The whole is well stirred and fused over a strong flame for 2 hrs. This will convert all barium sulphate into barium carbonate. The fused mass is cooled down and boiled with distilled water. The solution is filtered and the residue washed well with water. This is then dissolved in dilute HCl and the solution filtered if necessary. The barium will now be in the filtrate in the form of barium chloride. It is heated to the boil and the barium precipitated by the addition of a few c.cs. of 10 per cent. H_2SO_4. The barium sulphate is filtered, washed with hot distilled water, dried, ignited in a porcelain crucible and weighed as in $BaSO_4$.

Magnesium.—The total magnesium is determined by the following method. The ash from 5 gms. of leather is dissolved in dilute HCl and the solution boiled. An excess of ammonia is added, followed by a slight excess of a hot solution of ammonium oxalate. The precipitate, consisting of iron and aluminium hydrates and calcium oxalate is filtered off, washed well with distilled water and the filtrate, containing the magnesium evaporated to dryness in a platinum dish. The residue is carefully ignited to expel all ammonium salts, and dissolved in warm dilute HCl. The solution is made alkaline with a slight excess of ammonia. If a precipitate is formed it is re-dissolved in dilute HCl, and re-precipitated with dilute HCl. This will form *in situ* sufficient ammonium chloride to keep in solution the magnesium. The liquid is filtered if necessary and cooled. The magnesium is then precipitated with a slight excess of sodium phosphate solution. Precipitation is hastened by stirring the liquid vigorously. After standing overnight, the precipitate of magnesium ammonium phosphate is filtered off, washed with weak ammonia solution and dried in a steam oven. It is then ignited in a tared crucible and weighed as $Mg_2P_2O_7$ from which the weight of $MgSO_47H_2O$ can be calculated.

$$Mg_2P_2O_7 \text{ into } MgSO_47H_2O = 2{\cdot}214$$

For the estimation of sodium salts in leather the method given by Mann[13] is recommended. It is very rare, however, that excessive quantities of soda salts are found.

Soluble Ash—100 c.cs. of the water soluble matter is evaporated to dryness in a weighed porcelain or platinum dish and ignited until all carbonaceous matter has been driven off. The residual ash is then cooled and weighed. This gives the soluble ash in 2 gms. of original leather.

Insoluble Ash.—This is the difference between the total ash and soluble ash.

The Degree of Tannage.—The degree of tannage is the number of parts of tanning matter combined with 100 parts of Hide substance. Thus—

$$\frac{\text{Tannin combined} \times 100}{\text{Hide substance}}$$

The combined tannin is found by subtracting the sum of the percentages of moisture, fat, hide substance, insoluble ash and water soluble matter from 100. For details on this particular point the reader is referred to a paper by Parker and Paul.[14]

TABLE XII

COMPOSITION OF VARIOUS LEATHERS

(Parker and Paul)

Leather.	Remarks	Moist.	Total ash.	Insoluble ash.	Fat	Water soluble matter	Pure leather	Hide substance	Combined tannin	Degree of tannage.
English sole leather	No extract	17·08	0·59	0·29	0·84	20·0	61·77	35·37	26·4	74·6
Pine hemlock leather, U.S.A.	,,	17·06	0·74	0·27	0·89	17·4	64·32	38·50	25·82	67·0
Venezuela sole leather	,,	18·02	0·63	0·11	0·38	5·45	70·07	48·05	28·02	58·3
West of England	,,	17·22	0·86	0·12	1·09	20·20	61·32	35·00	26·32	75·2
Oak sole	,,	17·51	0·48	0·09	0·91	10·05	62·53	36·9	25·63	69·4
French pure oak	,,	18·08	0·79	0·07	0·11	7·28	74·33	42·0	31·73	74·4
Canadian hemlock	,,	16·52	0·88	0·13	2·06	15·1	66·30	33·6	32·7	97·3
English sole	Mixed tannage	15·6	1·02	0·18	0·8	16·6	66·7	35·6	31·10	87·3
French sole	,, ,,	16·34	1·31	0·12	0·95	17·5	65·0	39·2	25·8	65·8
German split	,, ,,	16·00	1·45	0·25	0·0	22·2	61·5	40·6	20·9	51·4
English sole (retanned)	,, ,,	16·4	2·4	0·14	1·3	10·9	63·2	35·05	28·15	80·3
English drum tanned	,, ,,	16·04	1·24	0·18	1·71	23·95	58·12	35·84	22·28	62·1
Spanish sole	,, ,,	18·26	1·16	0·14	0·18	11·75	69·56	40·55	29·01	71·5
German sole	Adulterated	17·6	2·2	0·18	1·6	22·3	58·2	34·4	23·8	69·1
German upper	,,	15·5	2·07	0·25	2·81	28·4	53·0	30·8	22·2	72·0
Belgian sole	,,	16·78	2·6	0·19	1·9	20·52	60·5	34·2	26·3	61·8
Italian sole	,,	17·1	1·91	0·17	1·8	21·4	59·5	35·6	23·9	67·1
American sole	,,	17·6	3·2	0·28	1·6	22·6	58·0	33·3	24·7	74·1
English sole	,,	17·86	4·82	0·15	1·37	10·9	53·75	43·3	20·45	47·2
Belgian sole	,,	17·9	4·95	0·21	1·2	23·8	56·83	33·8	23·03	68·1

Nature of Tanning Agent.—To detect the nature of the tanning material employed is a very difficult matter indeed, and not infrequently impossible. Very little work has been done on this particular subject, but the following table (Table XIII) from Procter,[15] worked out by Andreasch,[16] may be of use. The leather is extracted with alcohol and the solution tested with the various reagents as indicated. The tests are allowed to stand overnight and next day any characteristic colour or precipitate noted. The tests are rather uncertain where more than one tanning material has been used.

Sulphite Cellulose in Leather.—The detection of this material in leather is of considerable importance as it is viewed by many in the light of an adulterant. Moeller[17] adopts the following method. The leather in not too fine a state of division is extracted for about 24 hours in the cold with a 10 per cent. alcoholic solution of KOH. The solution is filtered off and the alcohol expelled by evaporation on the water bath. The residue is dissolved in water and the solution made acid with dilute sulphuric acid. The precipitate is filtered and the filtrate tested for sulphite cellulose by the Procter-Hirst reaction (see p. 118).

It has since been pointed out by Lauffman[18] that the artificial tanning material Neradol interferes with the above test, and recommends the following modification in order to distinguish between these two materials.

The finely divided leather is soaked overnight in a 2 per cent. solution of NaOH and filtered. The filtrate is made slightly acid with HCl and again filtered. The filtrate is tested by the Procter-Hirst reaction or the cinchonine test (see below). If this gives negative results it indicates the absence of both sulphite cellulose and Neradol. If positive, either may be present. A special test for Neradol must then be made. 3–4 drops of an ice-cooled solution of diazotised para-amino phenol is added to 5 c.cs. of the filtrate obtained above. A blue colour will indicate Neradol. The following test may also be made and is based on the separation of Neradol and sulphite cellulose with alcohol.

The solution to be tested is concentrated and mixed with alcohol. The precipitate is filtered off and the filtrate heated on the water bath to expel the alcohol. It is then diluted with water and made acid with H_2SO_4 to precipitate phlobaphenes, and again filtered. The filtrate is neutralised with Na_2CO_3 and treated with an excess of a 2½ per cent. solution of aniline hydrochloride. Neradol, if present, will give a

precipitate. The precipitate obtained after diluting the original solution with alcohol can be dissolved in distilled water and tested by the Procter-Hirst reaction for sulphite cellulose.

Appelius and Schmidt[19] use a solution of cinchonine as a reagent for sulphite cellulose. 5–10 gms. of the leather is extracted with 100 c.cs. of boiling water and the solution filtered. 5 c.cs. of 25 per cent. HCl is added to the filtrate which is again boiled and filtered. For each 50 c.cs. of filtrate is added 20 c.cs. of cinchonine solution and a little tannin solution. The former solution is prepared by dissolving 5 gms. of pure cinchonine in 100 c.cs. of distilled water and adding strong sulphuric acid drop by drop until a clear solution is formed. After adding the reagents, the mixture is heated without shaking until it boils. In the presence of even minute quantities of sulphite cellulose, a characteristic precipitate will be formed. It is characterised by forming a blackish-brown lumpy mass. It would be advisable to test a sample of leather of known purity at the same time as that actually under examination. A very weak solution of a cellulose extract could also be used as a guide to the character of the precipitate (cf. Seel and Sander).[20]

Microscopical Test.—Seel and Sander (*loc. cit.*) give the following method for the microscopical examination of leather in order to determine whether or not the sample is undertanned.

A thin section of the leather is stained with a basic dyestuff such as malachite green, methyl green, Bismarck brown and rhodamine, and the superfluous dye washed out with water and then alcohol. It is then counterstained with an acid dyestuff. The untanned part will be stained with the latter colour, while the fully tanned portion will be dyed with the basic colour.

(2) **Chrome Leather.**—The moisture, ash, fat and hide substance are determined by the method already given for vegetable tanned leather. The water soluble matter should be determined as this will give an idea as to whether such substance as glucose, etc., have been used.

Chromium.—1 gm. of the finely cut sample is ignited in a crucible and the ash cooled and intimately mixed with three or four times its weight of fusion mixture. This is prepared by mixing sodium and potassium carbonates in their molecular proportions. The whole is fused over a strong flame until green particles of chromic oxide are no longer visible. The mass is allowed to cool and the melt dissolved in hot water

[*Continued on p.* 170.

TABLE XIII.

Reagent.	Spruce bark.	Oak bark.	Willow bark.	Mimosa bark.	Hemlock bark.	Oakwood.
Water . .	Orange turbidity	Yell.-white ppt. partly soluble	Greenish turbidity	Yell.-white ppt. brown soln.	Dark-red brown ppt.	Light-yell. turbidity
Hydrogen peroxide .	As above	Yell.-white ppt. partly soluble	Apple-green ppt.	As above	Light-brown ppt. and soln.	Yell.-white flocculent ppt.
Hydrochloric acid . .	Red-brown soln.	Yell.-brown ppt. brown soln.	Yell.-white ppt. rose-red zone	As above	Dark-brown ppt. and soln.	Pale-buff flocculent ppt.
Sulphuric acid . .	Rust-brown ppt and soln.	Yell.-white ppt. brown soln.	Yell.-brown ppt. cherry-red zone	Slight rust-brown ppt. dark soln.	Dark rust-brown soln.	Brown ppt. and soln.
Nitric acid .	Yell.-brown ppt. dark-brown soln.	As above	Yell. ppt. and soln.	As above	Red-brown ppt. and soln.	Yell. flocculent ppt.
Acetic acid .	Yell.-white ppt.	—	—	—	—	-
Ammonia .	Brown ppt. partly sol. in excess	Dark-yell. ppt. sol. in excess	Turbidity	Violet-red ppt. sol. in soln.	Dark-brown ppt. insol. in excess	Ppt sol. in excess to red soln.
Chloroform .	Yell.-red flocculent ppt. brown soln.	Yell.-white ppt. yellowish soln.	Whitish turbidity	-	—	Dark-brown deposit
Ethyl ether .	Light brown ppt.	Light yell. ppt.	—	Grey-violet ppt.	Brown ppt.	Slight yell. white ppt.
Acetic ether	Turbidity	—	- -	-	—	—
Benzol . .	Reddish brown sediment	Brown flocculent ppt.		Reddish black layer	Brown layer below	Slight red brown ppt.
Petrol ether	Ether, not coloured	Ether pale yellow	—	—	Ether faint red	-
Carbon disulphide .	CS_2 yellow	CS_2 yellow	CS_2 green	CS_2 pale yellow	—	—
Naphthol .	Brown ppt. and soln.	Brown ppt. and soln.	Yell.-brown ppt. dark-red-brown soln.	Brown ppt. and soln.	—	Yell.-brown ppt. dark soln.
Glycerol .	Yell. flocculent ppt.	-	Greenish white flocculent ppt.	—	Red flocculent ppt.	Slight turbidity
Tartaric acid	Whitish yellow turbidity	Slight whitish yellow turbidity	Yell.-green flocks	Yell.-brown ppt.	Red-brown ppt.	Whitish yell. flocculent ppt.
Citric acid .	As above	As above	As above	As above	As above	As above
Oxalic acid .	As above	As above	As above	As above	Voluminous red-brown ppt.	As above
Trinitrophenol . .	Yell. ppt. and soln.	—	—	—	Yell.-brown ppt.	—

(*Andreasch.*)

Quebracho.	Valonia.	Myrobalans.	Divi-divi.	Sumach	Knoppern.	Birch bark.
Turbidity	Dirty yell., turbid over dark zone	Dirty yell. turbidity	Marked yell.-brown turbidity	Dirty green ppt.	Yell.-white ppt	Yell.-brown turbidity
Brown-yell. flocculent ppt.	As above	Yellowish ppt.	Yellowish ppt.	Green ppt.	As above	Rusty brown ppt.
As above	Light-brown turbidity	Light-brown turbidity	Whitish yell. ppt.	Dark green ppt.	As above	Yell.-brown ppt.
Dark-red soln.	Slight yell. ppt. pale soln.	Slight yell.-brown turbidity	Dirty red ppt.	Light green soln. and ppt.	Yell.-grey ppt.	Dense red-brown ppt. dark soln.
Slight ppt. red-brown soln.	Slight pale ppt. dark soln.	Dull red coloration	Dirty brown turbidity	Dark green ppt.	Dark yell. ppt.	Red-brown ppt. and soln.
	Yellowish turbidity	Dark-yell. turbidity	Light brown turbidity	Dull green ppt.	Yell.-brown ppt	—
Dark-red brown ppt.	Yell. ppt. partly sol. reddens	Yellowish ppt., turns brown, sol. in excess	Pale yell. ppt. partly sol. in excess, turns brown	Pale green ppt. darkened	Dense grey-white ppt., reddening	Dark flesh red ppt. sol. in excess
Soln. pale-yell. above red-brown	Yell.-grey flocks	Yell. flocks	Yell.-brown flocks	Slight green deposit	Dense yell.-white ppt.	Slight brown ppt
—	—	--	-	--	Grey-brown ppt	Trace flesh-coloured ppt.
---	—	—			—	-
—	Dirty white ppt. turning dark-brown	Pale-yell. flocks	Rust brown ppt.	Slight yell. ppt. on long standing	Reddish yell. flocks	—
---	-	—			Ether yell.-green	--
- -	Dense yell. flocks at zone	CS_2 scarcely coloured yellow flocks	CS_2 scarcely coloured yellow flocks	CS_2 coloured green	CS_2 coloured yell.-green	—
Yell.-brown ppt. dark soln.	Slight yell. brown ppt.	Slight yell. brown ppt.	Slight yell. brown ppt.	Green-brown ppt.	Slight grey ppt. on standing	Yell.-brown ppt. dark-red soln.
—	Long-standing yellowish ppt.	Long-standing yellowish flocks	Long-standing slight turbidity	Long-standing dark-green ppt	Slight turbidity	Turbidity
Yell.-brown flocculent ppt. dark-red soln.	Yell.-grey ppt.	Yellowish ppt.	Yellowish ppt.	Greenish ppt.	Yell. green ppt.	Light rust-brown ppt.
As above	As above	As above	As above	As above	As above	As above
As above	Sulphur-yell. ppt.	As above	Yell.-brown ppt.	As above	As above	As above
—	Brown-yell. ppt. turns lemon	Yell.-brown ppt. turns yellow	Turbidity first reddish, then yellow	Apple-green ppt.		

TABLE XIII.

Reagent.	Spruce bark.	Oak bark.	Willow bark.	Mimosa bark.	Hemlock bark.	Oakwood.
Salicylic acid	Light brown ppt.	Yell.-white flocculent ppt.	Greenish yell. ppt.	Slightly brown ppt.	Bulky red-brown ppt.	Yell.-white ppt.
Tartar emetic	Fawn-coloured ppt.	Greyish yell. ppt.	Greenish white ppt., deep green above layer	Violet-red ppt.	Dirty brown ppt.	As above
Potassium ferrocyanide	Yell.-white ppt.	Yell.-white ppt.	Green-white ppt.	Flesh red ppt.	Red-brown ppt.	Slight white ppt.
Potassium sulpho-cyanide	Yell.-brown flocculent ppt. sol. on heating	Yell.-brown flocculent ppt	Leaf green ppt.	Chocolate ppt.	Red-brown ppt. sol. on heating	Yell.-white ppt., pale yell. soln.
Potassium cyanide	Pale brown turbidity	Pale brown turbidity	Leaf green ppt., yell. soln.	—	As above	Ppt. brown below, yell.-white above
Lime	Yell.-brown ppt. glittering on surface	Ppt. yell.-brown below, chocolate above. Yell. soln.	Dirty sulphur yell. ppt.	Violet blue ppt., brown above	Violet-brown ppt., dull brown and glittering above	Ppt. white below, above blue, later brown
Baryta	Dirty yell. ppt., yell.-white soln.	As above	As above	Blue-green ppt., brown above	As above	Blue ppt., turning brown, glittering red-brown above
Strontia	As above	As above	As above	Dirty blue ppt.	As above	Ppt. white below, blue above, turning brown
Magnesia	Light brown ppt.	Dirty white ppt.	Violet-red ppt., green soln.	Grey ppt.	Red ppt.	Yell.-white ppt.
Potassium chromate	Dull brown ppt.	Yell.-brown ppt.	Bright yell. ppt.	Brown ppt.	Brown ppt.	Green-brown ppt., turning brown
Mercuric chloride	Light red-brown ppt.	Yell.-white turbidity	White ppt.	Light reddish blue ppt.	Blood red ppt.	Yell.-white flocculent ppt.
Mercurous nitrate	Dirty grey-brown ppt.	Ppt. reddish yell., turning brown	Dirty yell. ppt. on long standing	Dirty brown ppt.	Red-brown ppt., turning dull brown	Brick red ppt., turning brown-red or yell.-grey

(*Continued.*)

Quebracho.	Valonia.	Myrobalans.	Divi-divi.	Sumach.	Knoppern.	Birch bark.
Brown-yell. ppt., dark red-brown soln.	Greyish yell. ppt.	Yellowish ppt.	Yell.-brown ppt.	Green ppt.	Greyish yell. ppt.	Pale rust brown ppt.
Fawn-coloured ppt.	Pale grey-yell. ppt.	Cream-coloured ppt.	Ochre yell. curdy ppt.	Yell.-green curdy ppt.	Dirty white curdy ppt.	Bulky pale rusty ppt.
Pale red-brown ppt.	Pale yell. ppt.	Cream yell. ppt.	Orange ppt.	Pale green ppt	Yell.-green ppt.	As above
—	Yell.-grey ppt.	Yell. ppt.	Dark yell. ppt.	Green ppt.	Orange yell. ppt.	Turbidity
Slight ppt., amaranth red soln.	As above	As above	As above	As above	Curdy red-white ppt, darkens on standing.	Yell.-white ppt., dull brown, glittering above
Violet-brown ppt., dark brown above	Pale chocolate ppt.	Bright yell. ppt, colourless soln.	Cream colour ppt. darkens	Green ppt., turning yell.	Olive brown ppt.	Flesh red or scarlet ppt.
Grey-white ppt., glittering chocolate brown above	As above	As above	As above	Green ppt., turning sulphur yell.	Green ppt., turning grey-brown overnight	Grey-white ppt., brown above
As above	Chocolate ppt., turning black	Dirty green ppt., turning brown	Pale red ppt., dirty grey above	As above	As above	Greyish white ppt., vermilion above
Violet ppt., dark soln.	Yellowish ppt.	Yellowish ppt	Grey-brown ppt.	Dirty green mass	Yell.-white ppt.	Pale flesh ppt.
Dark, dull brown ppt.	Yell.-brown ppt.	Dirty brown ppt.	Dark brown ppt.	Dirty brown ppt.	Dark red violet ppt., turning chocolate	Chestnut brown ppt.
Dark turbidity	Dirty yell. ppt., partly soluble	Yell.-brown ppt., sol in excess	Brown ppt., mostly sol. in excess	Dirty green ppt., partly sol. in excess, turns yellow	Yell.-green ppt.	Reddish yell. ppt.
Chocolate ppt. on long standing	Orange yell. ppt., turning dirty yell.	Orange yell ppt., turning dirty yell.	Orange yell. ppt., turning dirty yell.	Grass green ppt.	Orange ppt., turning grey	Grey ppt.

and filtered. If any green chromic oxide is seen on the filter paper, the whole of the residue is dried in the steam oven, ashed, and again fused with fusion mixture. The yellow filtrate, containing the chromium in the form of alkali chromate, is made acid with an excess of HCl and cooled under the tap. This converts the chromate into chromic acid, which is then titrated with $\frac{N}{10}$ $Na_2S_2O_3$, after adding 1–2 gms. of potassium iodide. Starch paste is used as the indicator.

$$1 \text{ c.c. } \frac{N}{10} Na_2S_2O_3 = 0{\cdot}00253 \text{ gm. } Cr_2O_3.$$

Acid in Chrome Leather. -The estimation of free acid in chrome leather is a matter of difficulty as the Procter-Searle method (see p. 172) does not always give very satisfactory results with this class of leather. If used with care, however, results can be obtained which will, no doubt be somewhere near the correct figure.

The following procedure is suggested by Grasser[21] and will indicate over-neutralising as well as the presence of free acid.

20 gms. of the finely divided leather is made into a paste with 30 c.cs. of normal HCl or H_2SO_4, and the whole warmed for about an hour over a small flame, using a water-cooled reflux condenser. The condenser is washed down with a little distilled water and the solution titrated with normal NaOH, using methyl orange as indicator. If more than 30 c.cs. are required free acid is present and each c.c. over and above 30 c.c. corresponds to 0·049 gm. free H_2SO_4. If less than 30 c.cs. are needed, then the leather has been over-neutralised, *i.e.* free alkali is present. In this case, the 30 c.cs. minus the quantity of normal alkali required for titrating back will give the number of c cs. of normal acid corresponding to the free alkali present. This, for convenience, may be calculated into Na_2CO_3. 1 c.c. normal acid, 0·053 gm. Na_2CO_3.

Fahrion[22] applies the following test to chrome leather. 2 gms. of the leather is heated with 16 c.cs. of 8 per cent. alcoholic NaOH and the alcohol expelled by evaporating the mass to dryness. The residue is dissolved in HCl and again taken to dryness. The residue is re-dissolved in HCl diluted with hot distilled water and filtered. Ammonia is added to the filtrate to precipitate the chromium which is afterwards filtered off, washed with boiling distilled water, dried, ignited and weighed as Cr_2O_3. The filtrate from this determination

is made acid with HCl and the total sulphates estimated by precipitating with a hot solution of $BaCl_2$ (see p. 14).

From these two figures, the ratio $Cr_2O_3 : SO_3$ is calculated. As a standard, the ratio 1·56 : 1 is given.

Boiling Test.—A well-chromed leather will not alter in appearance when boiled for a short time in water. If it shrinks up when so treated, it is an indication that it is undertanned. Lamb and Harvey[23] say that a fully-chromed tanned leather will show at least 2·8–3 per cent. of Cr_2O_3 calculated on the degreased leather.

(3) **Light Leathers.**—The examination of light leathers is frequently undertaken with a view of finding out if possible its method of manufacture, and the additional notes given below will assist the student in this direction.

The ash of the sample will give some indication as to the nature of tannage. In the case of vegetable tanned leather the ash will be comparatively low, while chrome-tanned leather may show up to 5 per cent. of ash of which up to 4·5 per cent. will be chromic oxide. Alum-tanned leather will contain rather a high percentage of mineral matter consisting essentially of aluminium oxide. If only very small quantity of chromic oxide is present, say 0·2-0·3 per cent., it may be concluded that bichromate was used in the dyeing process. Iron oxide is found in leathers which have been dyed or toned down with an iron salt such as ferrous sulphate. This is very plainly seen in some samples by burning a small strip of the leather over a bunsen flame, when, on the grain side of the leather, a thin red film of Fe_2O_3 will be seen on the surface of the strip of ash. With black leathers, the presence of iron may indicate the combined use of iron salts and logwood in dyeing.

Pyrophosphate-tanned leather is distinguished by the presence in the ash of a quantity of phosphates, and at the same time the ash will be rather high. Barber and Barker[24] give the following figures from leathers tanned with the aid of phosphate of soda.

Tanned with Salt, Alum, Sodium Phosphate and Gambier.—

Ash	3–4 per cent.
PO_4 per cent. of ash . .	40–60 „
Al „ „	35–40 „

Tanned with Alum, Salt, and Sodium Phosphate.—

Ash	10 per cent.
PO_4 per cent. of ash . .	25 „
Al „ „ . .	20 „

Copper in very small traces may be found in some leathers where it has been used in the dyeing process.

Titanium, now largely used for dyeing purposes in the form of oxalate, etc., may be detected as follows. The ash from a few grams of the leather is fused for half an hour with potassium bi-sulphate. The melt is cooled, dissolved in water and filtered. A few drops of H_2O_2 are added to the filtrate. A yellow red colour indicates titanium.

For the estimation of the various ash constituents, the reader is referred to one of the standard books on inorganic analysis.

Free Mineral Acid.—The estimation of free mineral acid in leather is of importance in view of the destructive effect of even small quantities on the leather fibre. (On this point the reader should consult the Report on Bookbinding leathers issued by the Royal Society of Arts.)[25]

Many methods have been proposed for the estimation of free acid, but that most generally used is the Procter-Searle[26] method. 2 gms. of the finely divided leather is weighed into a porcelain basin and treated with 25 c.cs. of exactly $\frac{N}{10}$ Na_2CO_3. The mass is evaporated on the water bath, and then gently ignited to drive off all volatile organic matter. The ignition should not be carried too far, and should be stopped when no more fumes are evolved, and only a mass of carbon remains. It is then cooled down and extracted by boiling with a convenient quantity of distilled water. After boiling, the solution is filtered and the residue of carbon and the filter paper dried in the oven in the basin used for the evaporation and then ignited to a pure ash. This is cooled down and warmed slightly with exactly 25 c.cs. of $\frac{N}{10}$ H_2SO_4. The acid liquid is diluted and transferred to the filtrate obtained above. If the leather is quite neutral, this solution should also be neutral, as the 25 c.cs. of acid added will merely neutralise the 25 c.cs. of alkali added in the first instance. A few drops of methyl orange solution is added to the liquid and any acid present titrated with $\frac{N}{10}$ Na_2CO_3.

$$1 \text{ c.c. } \frac{N}{10} Na_2CO_3 = 0{\cdot}0040 \text{ gm. } H_2SO_4.$$

REFERENCES

[1] *Jour. Soc. Leather Trades Chem.*, 1918, p. 51.
[2] *Coll.*, 1911, p. 113.
[3] *Jour. Soc. Leather Trades Chem.*, 1918, p. 132.
[4] *Bull. Soc. Chim.*, 1908, p. 171.
[5] *J.S.C.I.*, 1909, p. 291.
[6] *Jour. Amer. Leather Chem. Assoc.*, 1918, p. 138.
[7] *Ibid.*, 1918, p. 313.
[8] *Ibid.*, p. 140.
[9] *Ibid.*, 1915, p. 445.
[10] *Coll.*, 1912, p. 162.
[11] *Jour. Amer. Leather Chem. Assoc.*, 1909, p. 250.
[12] *Coll.*, 1913, p. 308, also p. 504.
[13] *Jour. Soc. Leather Trades Chem.*, 1918, p. 19.
[14] *J.S.C.I.*, 1910, p. 315.
[15] "Laboratory Book," p. 315.
[16] *Gerber.*, 1894.
[17] *Abstr. Jour. Amer. Leather Chem. Assoc.*, 1915, p.
[18] *Abstr. J.S.C.I.*, 1917, p. 513.
[19] *Abstr. Coll.* (London Edition), 1916, p. 288.
[20] *Ibid.* (London Edition), 1917, p. 48.
[21] *Coll.*, 1910, p. 381.
[22] *Ibid.*, 1911, p. 205.
[23] *Ibid.* (London Edition), 1916, p. 201.
[24] *Jour. Soc. Leather Trades Chem.*, 1917, p. 102.
[25] "Report of the Society of Arts Committee on Leathers for Bookbinding."
ll & Sons. 1905.
[26] *Coll.*, 1906, p. 298.

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CHAPTER XVIII

FINISHING MATERIALS

THE following notes on the various sizing and finishing materials used in the leather trade will assist in determining the purity of commercial samples.

Albumin. Egg and blood albumins are both used in the leather trade, the former being favoured on account of its usual light colour and freedom from iron. When a solution of either is applied to the leather, the film formed is capable of taking a very high polish when glazed.

Commercial samples are examined for moisture, ash, and albumin. This latter is obtained by multiplying the percentage of nitrogen found by the Kjeldahl method by the factor 6·37.

The following, according to Lamb and Harvey,[1] represent the composition of average samples of albumin :—

BLOOD ALBUMIN.

Moisture	= 21·35 per cent.	24·53 per cent.
Ash and mineral matter	= 8·41 ,,	9·06 ,,
Albumin	= 70·13 ,,	65·73 ,,
	99·89 ,,	99·32 ,,
Nitrogen	11·01 ,,	10·32 ,,
Colour	Straw yellow	Brown

EGG ALBUMIN.

Moisture	= 25·94 per cent.
Ash (white fusible)	= 4·69 ,,
Albumin	= 69·30 ,,
	99·93

Both blood and egg albumin should be completely soluble in a 1 per cent. solution of NaOH, while very little insoluble matter should be left when 1-2 gms. of the sample is allowed

to soak in water for 5–10 hours. Albumins which have been dried at a too high temperature during manufacture will be almost insoluble in water. Blood albumin dissolves in strong HNO_3 whereas egg albumin is very slowly soluble. The ash from both varieties should be examined for iron as this is a very undesirable constituent, especially when the albumin is to be used as a finish on light shades.

Liquid albumins are frequently treated with zinc salts which act as preservatives, and at the same time increase the viscosity of the solution. Such addition can be detected by examining the ash for zinc by the usual qualitative tests.

Irish Moss.—This excellent finishing material contains 1·4 per cent. to 2·5 per cent. of nitrogen as estimated by the Kjeldahl method. The amount of ash present will vary within wide limits according to the care exercised in its preparation. A large proportion will be common salt, and can be estimated by titrating the aqueous extract of the ash with $\frac{N}{10}$ silver nitrate solution. In this determination, more satisfactory results will be obtained if the sample is ignited until the organic matter is destroyed and not taken to complete ash. The carbonaceous matter is then extracted with hot water, and the extract titrated with standard silver nitrate solution. By this means loss of chlorides by volatilisation is avoided.

An analysis by Lamb and Harvey (*loc. cit.*) is given below.

IRISH MOSS.

Moisture	= 20·9 per cent.
Ash	= 18·38
Nitrogen	= 1·58

Gum Tragacanth.—This is liable to adulteration with inferior gums on account of its high price. The percentage of ash varies from 2–3·0 per cent. and the moisture from 18–22 per cent.

Adulteration with Indian Gum can be detected by a distillation test devised by Emery.[2] This is based on the fact that genuine tragacanth gives very little volatile acid when distilled in the presence of phosphoric acid.

A known weight of the gum is introduced into a distillation flask together with a convenient volume of water and an excess of phosphoric acid. The whole is allowed to stand overnight and the volatile acid distilled over, using a Liebig

condenser. The distillate is then titrated with $\frac{N}{10}$ NaOH, using phenol phthalein as indicator. The acidity is calculated as acetic acid.

$$1 \text{ c.c. } \frac{N}{10} \text{NaOH} = 0{\cdot}006 \text{ gm. acetic acid.}$$

Genuine gum tragacanth will show an acidity of only about 2 per cent., whereas samples adulterated with Indian gums will show a much higher figure, in some cases over 8 per cent.

Ferric chloride does not give a precipitate with an aqueous solution of the gum, but alcohol throws it out of solution in the form of a mass of clots.

Payet[3] gives the following test for the detection of gum arabic in tragacanth. A small quantity of a 3 per cent. solution of the gum in water is treated with an equal volume of a 1 per cent. aqueous guaiacol solution and one drop of hydrogen peroxide. Pure tragacanth will remain colourless, while the presence of gum arabic will be indicated by the formation of a brown colour. The test is based on the fact that gum tragacanth contains no active oxidase such as is present in gum arabic.

Another test depends upon the solubility of gum arabic and the insolubility of tragacanth in an ammoniacal solution of copper oxide.[4]

Gum Arabic.—This gum is obtained from various species of the acacias, *e.g.* Acacia senegal, A. horrida, etc.

Analyses by Lamb and Harvey gave the following results :—

Moisture	4·1 per cent.	18·07 per cent.
Ash	2·4 „	2·66 „

Not more than 4 per cent. of ash should be present and the quantity insoluble in water should be very small. Pure gum arabic is not precipitated by normal lead acetate and does not give a blue coloration with iodine solution showing freedom from starch. If boiled with Fehling's solution very little reduction takes place.

Casein.—A good commercial casein should be of a pale yellow colour and free from rancid odour. The following determinations should be made: moisture, ash, fatty matter, proteins.

The moisture is estimated by drying 4–5 gms. in the steam oven until no further loss in weight takes place. If

this is done in a platinum dish the dried residue can be used for the determination of the ash. The fat is determined by extracting 10 gms. of the sample with petrol ether in a Soxhlet apparatus for about 4 hours. The extracted fat is dried in the steam oven and weighed. The nitrogen is estimated by the Kjeldahl method, and the percentage found multiplied by the factor 6·61 to give the actual casein. To test for solubility, 10 gms. of the sample is treated with 50 c.cs. of distilled water to which has been added 2 c.cs. of a 30 per cent. solution of ammonia. The mixture is well stirred and allowed to stand for a short time. It is then warmed to about 60° C. when it should give a thick opalescent solution.

Examination of Manufactured Seasoning Compounds.—This presents a matter of difficulty, but the following determinations will assist in obtaining some information as to its probable composition.

10–20 gms of the sample is evaporated to dryness in a platinum dish and the residue of solid matter dried and weighed. This will give the total solids. The residue after weighing is ignited and the ash cooled and weighed. This is examined for iron and borax.

The determination of total nitrogen will give an idea as to the presence of such nitrogenous matter as casein, albumin, etc.

Free ammonia is determined by diluting a known volume of the season with water and distilling the ammonia into boric acid solution. The ammonia collected is then titrated direct with standard acid, using Congo red as indicator. The season need not be made alkaline before distillation.

Dextrin.—The following information on dextrin is taken from a paper on the subject by Lamb and Harvey.[5]

Moisture and Ash.—5–6 gms. of the sample are dried at 100° C. in an air oven, the dish being supported on a glass tripod. Four hours' heating will be found sufficient to give constancy of weight.

The ash is estimated in the usual way.

Water Soluble Matter.—10 gms. of the sample is shaken with cold distilled water in a 500 c.c. graduated flask and allowed to stand overnight. The solution is then made up to the 500 c.c. mark, well shaken and filtered. 50 c.cs. of the filtrate is evaporated to dryness in a weighed dish and the residue dried in the steam oven and weighed. This gives the total soluble matter in 1 gm. of the original dextrin.

Reducing Sugars.—Reducing sugars are estimated in 50 c.cs. of the above filtrate by means of Fehling's solution.

The sugar is calculated as dextrose, maltose only being present in dextrins manufactured by the diastase process.

Starch.—Starch is examined for qualitatively in the residue insoluble in cold water. This is washed with cold water and then transferred to a test tube and dissolved by boiling with a few c.cs. of water. The liquid is tested for starch by the iodine test.

The following are analyses of various samples of commercial dextrins:—

TABLE XIV

	(a)	(b)	(c)	(d)	(e)
Moisture	11·46%	7·21%	3·12%	6·13%	9·96%
Water soluble matter[1]	48·4	92·7%	96·65%	93·80%	89·90%
Ash	0·31	0·10	0·24	0·21	0·10
Dextrose	8·41	traces	traces	traces	traces
Starch	present	—	—	—	—

REFERENCES

[1] *J. Soc. Dyers Cols.*, 1917, No. 2.
[2] *J. Ind. Eng. Chem.*, 1912, p. 374.
Ann. Chim. Analyt., 1905, p. 63.
[4] *J.S.C.I.*, 1913, p. 1080.
[5] *J. Soc. Dyers Cols.*, 1918, No. 1.

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CHAPTER XIX

NATURAL DYESTUFFS

Of the large number of natural colouring-matters still used in the various dyeing industries only logwood and fustic are of any importance for the purposes of leather dyeing.

Logwood (Campeachy).—The greater part of the logwood now used is in the form of an extract, which is more convenient and cleaner to use than the wood itself.

Such extracts are sold under various names such as Hæmatine, Hæmatine crystals, etc.

A good logwood extract has a deep reddish black colour and is, as a rule, very free from extraneous matter. An aqueous solution gives a violet red colour with NaOH and a purple black with Fe_2Cl_6. Alum gives a very rich plum colour, which develops somewhat slowly.

Moisture.—Solid logwood extract contains about 10–12 per cent. of moisture, which is estimated in the usual way by drying a known amount in the steam oven.

Ash.—About 2 per cent. of ash is present in dry extracts, of which, according to Savini,[1] 25 per cent. is potash. If more than this amount of ash is present, coupled with an excessive quantity of potash, it is probable that the material has been adulterated with molasses.

The alkalinity of the ash corresponds to 60–71 c.cs. of $\frac{N}{10}$ acid per 100 gms. of extract (Savini).

Adulteration with Chestnut Extract.—Houzeau's method for the detection of chestnut extract is as follows: 1–2 gms. of the sample is dried at 100° C. and the residue extracted with pure dry ether. The etheral solution is evaporated to dryness in a weighed flask and the residue dried and weighed. The insoluble matter is then extracted with absolute alcohol and the alcoholic solution evaporated to dryness and the residue dried and weighed.

Genuine logwood extract contains about 87 per cent. of ether soluble substances and 12–14 per cent. of alcohol

solubles. The presence of chestnut extract diminishes the etheral extract and increases the alcohol soluble matter.

Nitrogen.—Dry logwood extract contains only small amount of nitrogenous matter, the percentage of nitrogen being about 1 per cent.

Dyeing Trial.—In order to arrive at a more definite opinion as regards a sample of logwood extract for the leather trade, a dye trial should be made on wool.

Wool Trial.—A good quality fat-free white wool is boiled with water for a short time to wash out any dressing, etc., and then mordanted with potassium bi-chromate. The mordanted wool is dyed with a definite amount of the extract to be tested. A comparative trial should be made at the same time, using an extract of known purity. For laboratory experiments, the following quantities will be found convenient:—

Wool	5 gms.
Potassium bichromate (15 c.cs. of a 1 per cent. soln.)	0·15 gm.
Water	300 c.cs.

The bichromate is dissolved in water and diluted to about 300 c.cs. This solution is heated, the wool entered, and the whole heated to the boil for about three-quarters of an hour, at the end of which time the wool is taken out, rinsed and dyed in the following bath:—

Logwood extract	1 gm.
Water	300 c.cs.

The wool is dyed for three-quarters of an hour at 100° C. and then washed out in warm water and dried. A good extract will give a black shade. It is better to work two trials, one as above and another using only half the amount of extract. The shades obtained, compared with those from an extract of known quality (and one which is known to give good results under factory conditions), will, as a rule, give all the information desired.

Logwood extract, also, has certain tanning properties, and an analysis of a liquid extract made by the American method for the examination of tanning materials gave the following figures:—[2]

Tannin	23·90
Non tannins	20·79
Insolubles	0·14
Moisture	55·17

Fustic Extract.—Fustic extract may be examined on lines similar to those given for logwood extract.

Fustic is frequently treated with zinc salts. These can be detected in the ash by extracting with HNO_3 and testing for zinc by the usual qualitative tests.

Turmeric may also be added. This may be detected by a dye trial. A skein of fat-free wool is dyed in a solution of the extract for half an hour at the boil and then taken out and rinsed. If the wool is dyed, turmeric, or perhaps a coal tar colour, is present. Pure fustic does not dye unmordanted wool. If alum is present in the extract the wool will be dyed as it will act as a mordant, so that before testing for turmeric the presence or not of alum should be ascertained by an examination of the ash.

REFERENCES

[1] *Ann. di Chim. Appl.*, 1917, p. 26.
[2] *Jour. Amer. Leather Chem. Assoc.*, 1913, p. 274.

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CHAPTER XX

COAL TAR DYES

COAL tar dyes are now used to a very large extent for the dyeing and staining of leather, and of course it is of importance that dyes used for these purposes should be of a uniform standard quality. In this respect, however, the standard products now being put on the market by British dyestuff manufacturers are very uniform as regards tinctorial properties, and provided that a comparative dye trial is made on each delivery to make sure that it is up to standard, there is very little else to be done in the way of examination.

In the examination of these colours, the Lovibond tintometer will be found very convenient for rapid testing, and if a record of tintometer readings be kept of each sample, it will indicate any great change in colour. It is essential, of course, to examine solutions of the same strength. As an example, the present author gives tintometer readings of different makes of nigrosine. 0·5 gm. of the sample was dissolved in distilled water and the solution made up to 500 c.cs. in a graduated flask. 20 c.cs. of this solution was further diluted to 500 c.cs. and the colour as measured by the tintometer recorded.

	Red.	Yellow.	Blue.
Sample 1	1·0	0·5	3·0
Sample 2	1·0	0·0	4·1
Sample 3	0·5	0·0	3·6
Sample 4	0·4	0·2	3·4

It is mentioned in passing that all the above samples were of different make.

Dye Trials.—1. *Direct Cotton Colours.*—A number of direct cotton colours are now being used for the dyeing of chrome

tanned leather, so that it is advisable to test these dyes on this type of leather.

A piece of chrome tanned calf weighing 10 gms. is soaked in water at about 60° C. until it becomes fairly evenly soaked. It is not possible to wet back chrome leather completely once it has been dried out, but half an hour at 60° C. will render the leather suitable for the trial

The wet leather is drained for a short time and then dyed with 0·1 gm. of the dyestuff dissolved in about 500 c.cs. of water. An addition of 2–3 gms. of sodium sulphate is made to the dyebath, and dyeing carried out at a temperature of 60° C. for three-quarters of an hour. In doing a number of trials at the same time, the beakers containing the dye solutions are placed in a water bath which is heated to the required temperature.

After dyeing, the leather is taken out of the dye solution, washed in warm water and then dried out.

The quantities of dye, etc., used correspond on a practical scale to 1 per cent. dyestuff and 20–30 per cent. Glauber salt.

The addition of this salt is necessary in order to aid the deposition of the dyestuff in an even manner on the leather. In some cases, such a large amount of Glauber salt will not be required, while there are some instances where dyeing proceeds satisfactorily without it. These facts can be ascertained by experiment.

2. *Acid Dyestuffs.* In dyeing with acid colours the only addition to the dye solution is a small quantity of an acid, which is required to liberate the colour acid.

Comparative trials are best done on skiver, *i.e.* the grain half of a split sheep skin tanned with sumach.

A piece of the skiver weighing about 10 gms. is wetted back by soaking in water at a temperature of 45° C. for 10 minutes. It is then slicked out with a glass slicker to remove superfluous water. 0·1 gm. of the dye is dissolved in a little warm water (boiling if necessary) and added to about 300 c.cs. of water at 45° C. 1 c.c. of 10 per cent. H_2SO_4 is then added and the leather introduced and dyed for three-quarters of an hour. The experiment is best made in a bottle which can be tightly corked and shaken in a mechanical shaker at a slow rate. This imitates, to a certain extent, the drum or paddle method of dyeing which is gradually becoming the most popular process. After dyeing, the leather is washed in warm water, slicked out and pinned flat on a board to dry.

If the shade obtained is too light, the trial is repeated, using 0·2 gm. of dye.

3. *Basic Colours.*—In testing basic colours it will be found necessary to fix the tannin in the leather by a preliminary mordanting. For this purpose tartar emetic (Antimony potassium tartrate) can be used. A piece of skiver weighing about 10 gms. is wetted back in warm water for 10 minutes and then slicked out. It is then mordanted in a bath containing 0·5 gm. of tartar emetic and 2 gms. of common salt dissolved in a convenient quantity of water, *e.g.* 300–400 c.cs. The leather is mordanted for half an hour at 45° C. at the end of which time it is taken out and rinsed in water and allowed to drain.

The dyebath is prepared using 0·1 gm. of the dye sample and enough acetic acid to neutralise the hardness of the water used with a slight excess to leave the bath faintly acid to litmus paper. The leather is then dyed in this bath for three-quarters of an hour at a temperature of 45° C., washed in warm water, slicked out, and pinned on a board to dry. The actual dyeing may be done either by suspension, *i.e.* the leather hung on two small copper hooks and suspended in the dyebath from a glass rod or by gentle shaking in a mechanical shaker.

In the above trials the question of price of the dye is not taken into consideration and the results obtained from a number of trials of say different make of the same dye only indicate the shade irrespective of cost. Further details on the method of conducting dyeing experiments are given in Lamb's treatise on "Leather Dressing."[1]

The quantity of dye used in the trials will vary to a certain extent according to the sample, but such details can be altered according to the wish of the operator. It is always best to calculate the weight of dye used on the weight of leather taken, as such gives information of direct practical value.

The fastness to light of the shade is of importance, and a test on this point should be made when new makes of dye are being examined. A piece of the leather dyed as in the above trials, is placed with the grain side uppermost in an ordinary photographic printing frame and exposed to light. The rate of fading can be noted. Lamb (*loc. cit.*) has made a large number of tests on this point and his results should be consulted.

Distinction between Acid and Basic Dyes.—A dilute solution of tannin containing a little sodium acetate is added to a weak solution of the dyestuff. Basic colours give a precipitate, while in the case of acid colours, the solution remains quite clear.

Mixtures.—Mixtures of two or more colours may be detected as follows:—1. A little of the colour is blown from a spatula on to a sheet of wet filter paper held about a foot away. The dye particles will settle on the paper and form coloured spots which will correspond to the colour of the different dyes present.

2. A small quantity of the dye is sprinkled on to the surface of a dish of alcohol. With mixtures streaks of various colours will be formed.

3. Some of the dye is sprinkled on to concentrated sulphuric acid and the various coloured streaks noted.

4. A few strips of filter paper are suspended in a dilute solution of the dyestuff so that their lower ends just dip into the solution. In the case of mixtures different coloured zones will be produced on the filter papers.

As regards the identification of a particular dyestuff, such standard works as Green's[2] should be consulted.

For the valuation of many coal tar dyes, use may be made of the reducing properties of titanous chloride. Full details as to the method will be found in the numerous papers published by Knecht and Hibbert in the *Journal of Society of Dyers and Colourists.* These have now been published in the more convenient form of a monograph.[3]

REFERENCES

[1] "Leather Dressing," 2nd edition, 1909.
[2] "The Analysis of Dyestuffs," 1915.
[3] "New Reduction in Volumetric Analysis," re-issue, 1918.

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APPENDIX

COMPARISON OF THE BAUMÉ AND TWADDLE DEGREES WITH THE SPECIFIC GRAVITIES

(Cain).

Bé.	Tw.	S.G.	Bé.	Tw.	S.G.	Bé.	Tw.	S.G.
0	0	1·000	15·4	24·0	1·120	29·3	51·0	1·255
0·7	1·0	1·005	16·0	25·0	1·125	29·7	52·0	1·260
1·0	1·4	1·007	16·5	26·0	1·130	30·0	52·6	1·263
1·4	2·0	1·010	17·0	26·8	1·134	30·2	53·0	1·265
2·0	2·8	1·014	17·1	27·0	1·135	30·6	54·0	1·270
2·1	3·0	1·015	17·7	28·0	1·140	31·0	54·8	1·274
2·7	4·0	1·020	18·0	28·4	1·142	31·1	55·0	1·275
3·0	4·4	1·022	18·3	29·0	1·145	31·5	56·0	1·280
3·4	5·0	1·025	18·8	30·0	1·150	32·0	57·0	1·285
4·0	5·8	1·029	19·0	30·4	1·152	32·4	58·0	1·290
4·1	6·0	1·030	19·3	31·0	1·155	[illegible]·8	59·0	1·295
4·7	7·0	1·035	19·8	32·0	1·160	33·0	59·4	1·297
5·0	7·4	1·037	20·0	32·4	1·162	33·3	60·0	1·300
5·4	8·0	1·040	20·3	33·0	1·165	33·7	61·0	1·305
6·0	9·0	1·045	20·9	34·0	1·170	34·0	61·6	1·308
6·7	10·0	1·050	21·0	54·2	1·171	34·2	62·0	1·310
7·0	10·2	1·052	21·4	35·0	1·175	34·6	63·0	1·315
7·4	11·0	1·055	22·0	36·0	1·180	35·0	64·0	1·320
8·0	12·0	1·060	22·5	37·0	1·185	35·4	65·0	1·325
8·7	13·0	1·065	23·0	38·0	1·190	35·8	66·0	1·330
9·0	13·4	1·067	23·5	39·0	1·195	36·0	66·4	1·332
9·4	14·0	1·070	24·0	40·0	1·200	36·2	67·0	1·335
10·0	15·0	1·075	24·5	41·0	1·205	36·6	68·0	1·340
10·6	16·0	1·080	25·0	42·0	1·210	37·0	69·0	1·345
11·0	16·6	1·083	25·5	43·0	1·215	37·4	70·0	1·350
11·2	17·0	1·085	26·0	44·0	1·220	38·7	71·0	1·355
11·9	18·0	1·090	26·4	45·0	1·225	38·0	71·4	1·357
12·0	18·2	1·091	26·9	46·0	1·230	38·2	72·0	1·360
12·4	19·0	1·095	27·0	46·2	1·231	38·6	73·0	1·365
13·0	20·0	1·100	27·4	47·0	1·235	39·0	74·0	1·370
13·6	21·0	1·105	27·9	48·0	1·240	39·4	75·0	1·375
14·0	21·6	1·108	28·0	48·2	1·241	39·8	76·0	1·380
14·2	22·0	1·110	28·4	49·0	1·245	40·0	76·6	1·383
14·9	23·0	1·115	28·8	50·0	1·250	40·1	77·0	1·385
15·0	23·2	1·116	29·0	50·4	1·252	40·5	78·0	1·390

I— (*continued*)

Bé.	Tw.	S.G.	Bé.	Tw.	S.G.	Bé.	Tw.	S.G.
40·8	79·0	1·395	50·9	109·0	1·545	59·5	140·0	1·700
41·0	79·4	1·397	51·0	109·2	1·546	59·7	141·0	1·705
41·2	80·0	1·400	51·2	110·0	1·550	60·0	142·0	1·710
41·6	81·0	1·405	51·5	111·0	1·555	60·2	143·0	1·715
42·0	82·0	1·410	51·8	112·0	1·560	60·4	144·0	1·720
42·3	83·0	1·415	52·0	112·6	1·563	60·6	145·0	1·725
42·7	84·0	1·420	52·1	113·0	1·565	60·9	146·0	1·730
43·0	84·8	1·424	52·4	114·0	1·570	61·0	146·4	1·732
43·1	85·0	1·425	52·7	115·0	1·575	61·1	147·0	1·735
43·4	86·0	1·430	53·0	116·0	1·580	61·4	148·0	1·740
43·8	87·0	1·435	53·3	117·0	1·585	61·6	149·0	1·745
44·0	87·6	1·438	53·6	118·0	1·590	61·8	150·0	1·750
44·1	88·0	1·440	53·9	119·0	1·595	62·0	150·6	1·753
44·4	89·0	1·445	54·0	119·4	1·597	62·1	151·0	1·755
44·8	90·0	1·450	54·1	120·0	1·600	62·3	152·0	1·760
45·0	90·6	1·453	54·4	121·0	1·605	62·5	153·0	1·765
45·1	91·0	1·455	54·7	122·0	1·610	62·8	154·0	1·770
45·4	92·0	1·460	55·0	123·0	1·615	63·0	155·0	1·775
45·8	93·0	1·465	55·2	124·0	1·620	63·2	156·0	1·780
46·0	93·6	1·468	55·5	125·0	1·625	63·5	157·0	1·785
46·1	94·0	1·470	55·8	126·0	1·630	63·7	158·0	1·790
46·4	95·0	1·475	56·0	127·0	1·635	64·0	159·0	1·795
46·8	96·0	1·480	56·3	128·0	1·640	64·2	160·0	1·800
47·0	96·6	1·483	56·6	129·0	1·645	64·4	161·0	1·805
47·1	97·0	1·485	56·9	130·0	1·650	64·6	162·0	1·810
47·4	98·0	1·490	57·0	130·4	1·652	64·8	163·0	1·815
47·8	99·0	1·495	57·1	131·0	1·655	65·0	164·0	1·820
48·0	99·6	1·498	57·4	132·0	1·660	65·2	165·0	1·825
48·1	100·0	1·500	57·7	133·0	1·665	65·5	166·0	1·830
48·4	101·0	1·505	57·9	134·0	1·670	65·7	167·0	1·835
48·7	102·0	1·510	58·0	134·2	1·671	65·9	168·0	1·840
49·0	103·0	1·515	58·2	135·0	1·675	66·0	168·4	1·842
49·4	104·0	1·520	58·4	136·0	1·680	66·1	169·0	1·845
49·7	105·0	1·525	58·7	137·0	1·685	66·3	170·0	1·850
50·0	106·0	1·530	58·9	138·0	1·690	66·5	171·0	1·855
50·3	107·0	1·535	59·0	138·2	1·691	66·7	172·0	1·860
50·6	108·0	1·540	59·2	139·0	1·695	67·0	173·0	1·865

II

Specific Gravity of Caustic Soda Solutions at 15° C.

(Lunge)

S.G.	NaOH.	S.G.	NaOH.
1·007	0·61	1·220	19·58
1·014	1·20	1·231	20·59
1·022	2·00	1·241	21·42
1·029	2·70	1·252	22·64
1·036	3·35	1·263	23·67
1·045	4·00	1·274	24·81
1·052	4·64	1·285	25·80
1·060	5·29	1·297	26·83
1·067	5·87	1·308	27·80
1·075	6·55	1·320	28·83
1·083	7·31	1·332	29·93
1·091	8·00	1·345	31·22
1·100	8·68	1·357	32·47
1·108	9·42	1·370	33·69
1·116	10·06	1·383	34·96
1·125	10·97	1·397	36·25
1·134	11·84	1·410	37·47
1·142	12·64	1·424	38·80
1·152	13·55	1·438	39·99
1·162	14·37	1·453	41·41
1·171	15·13	1·468	42·83
1·180	15·91	1·483	44·38
1·190	16·77	1·498	46·15
1·200	17·67	1·514	47·60
1·210	18·58	1·530	49·02

III

Specific Gravity of Sodium Carbonate Solutions at 15° C.
(Lunge)

S.G.	Na_2CO_3	% $Na_2CO_3 . 10 H_2O$.
1·007	0·67	1·807
1·014	1·33	3·587
1·022	2·09	5·637
1·029	2·76	7·444
1·036	3·43	9·251
1·045	4·29	11·570
1·052	4·94	13·323
1·060	5·71	15·400
1·067	6·37	17·180
1·075	7·12	19·203
1·083	7·88	21·252
1·091	8·62	23·248
1·100	9·43	25·432
1·108	10·19	27·482
1·116	10·95	29·532
1·125	11·81	31·851
1·134	12·61	34·009
1·142	13·16	35·493
1·152	14·24	38·405

IV

Specific Gravity of Sodium Sulphide Solutions
(Lamb and Holyoak)

S.G. of solution.	$Na_2S.9H_2O$.	S.G. of solution.	$Na_2S.9H_2O$.	S.G. of solution.	$Na_2S.9H_2O$.
1·003	1	1·066	21	1·123	41
1·006	2	1·068	22	1·126	42
1·010	3	1·071	23	1·129	43
1·013	4	1·074	24	1·132	44
1·017	5	1·077	25	1·134	45
1·020	6	1·080	26	1·137	46
1·023	7	1·083	27	1·139	47
1·027	8	1·086	28	1·141	48
1·030	9	1·089	29	1·144	49
1·033	10	1·092	30	1·146	50
1·036	11	1·095	31	1·149	51
1·039	12	1·098	32	1·152	52
1·042	13	1·100	33	1·155	53
1·045	14	1·103	34	1·158	54
1·049	15	1·106	35	1·161	55
1·052	16	1·109	36	1·164	56
1·055	17	1·112	37	1·167	57
1·058	18	1·115	38	1·169	58
1·061	19	1·118	39	1·172	59
1·064	20	1·120	40	1·175	60

V

Specific Gravity of Ammonia Solutions at $\frac{60°}{60°}$ F.

(Ferguson)

S.G.	NH_3.	S.G.	NH_3.	S.G.	NH_3.
1·0000	0·00	0·9556	11·18	0·9150	23·52
0·9982	0·40	0·9540	11·64	0·9135	24·01
0·9964	0·80	0·9524	12·10	0·9121	24·50
0·9947	1·21	0·9508	12·56	0·9106	24·99
0·9929	1·62	0·9492	13·02	0·9091	25·48
0·9912	2·04	0·9475	13·49	0·9076	25·97
0·9894	2·46	0·9459	13·96	0·9061	26·46
0·9876	2·88	0·9444	14·43	0·9047	26·95
0·9859	3·30	0·9428	14·90	0·9032	27·44
0·9842	3·73	0·9412	15·37	0·9018	27·93
0·9825	4·16	0·9396	15·84	0·9003	28·42
0·9807	4·59	0·9380	16·32	0·8989	28·91
0·9790	5·02	0·9365	16·80	0·8974	29·40
0·9773	5·45	0·9349	17·28	0·8960	29·89
0·9756	5·88	0·9333	17·76	0·8946	30·38
0·9739	6·31	0·9318	18·24	0·8931	30·87
0·9722	6·74	0·9302	18·72	0·8917	31·36
0·9705	7·17	0·9287	19·20	0·8903	31·84
0·9689	7·61	0·9272	19·68	0·8889	32·34
0·9672	8·05	0·9256	20·16	0·8875	32·83
0·9655	8·49	0·9241	20·64	0·8861	33·32
0·9639	8·93	0·9226	21·12	0·8847	33·81
0·9622	9·38	0·9211	21·60	0·8833	34·30
0·9605	9·8[illegible]	0·9195	22·08	0·8819	34·79
0·9589	10·28	0·9180	22·56	0·8805	35·28
0·9573	10·73	0·9165	23·04		

VI

SPECIFIC GRAVITY OF POTASSIUM BICHROMATE SOLUTIONS AT 19.5° C.

(Kremers and Gerlach)

S.G.	$K_2Cr_2O_7$	S.G.	$K_2Cr_2O_7$	S.G.	$K_2Cr_2O_7$	S.G.	$K_2Cr_2O_7$
1·007	1·0	1·037	5·0	1·065	9·0	1·095	13·0
1·015	2·0	1·043	6·0	1·073	10·0	1·102	14·0
1·022	3·0	1·050	7·0	1·080	11·0	1·110	15·0
1·030	4·0	1·056	8·0	1·087	12·0		

VII

SPECIFIC GRAVITY OF SODIUM BICHROMATE SOLUTIONS

(Stanley)

S.G.	$Na_2Cr_2O_7$	S.G.	$Na_2Cr_2O_7$	S.G.	$Na_2Cr_2O_7$
1·007	1	1·141	20	1·280	40
1·035	5	1·171	25	1·313	45
1·071	10	1·208	30	1·343	50
1·105	15	1·245	35		

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